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Supporting Information

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Regioselective Wacker Oxidation of Internal Alkenes: Rapid Access to Functionalized Ketones Facilitated by Cross-Metathesis**

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Supporting Information

General procedure:

All olefin oxidation reactions were carried out under aerobic conditions. Commercial reagents were obtained from Aldrich and used without further purification.

^{1}H and ^{13}C NMR spectra were recorded on a Varian 500 Mhz spectrometer and High resolution mass spectra were provided by the California Institute of Technology Mass Spectrometry Facility using JEOL JMS-600H High Resolution Mass Spectrometer.

Substrates in Table 1, Entries 1 and 4 were prepared by standard benzylation using NaH and BnBr in THF. Substrates in Table 1, Entries 2 and 5, as well as substrates in Scheme 5, were prepared by treatment of the corresponding alcohol with the corresponding benzoyl chloride in CH_2Cl_2 with 1.5 eq. pyridine. Catalyst **1** and **2** are commercially available from Sigma-Aldrich.

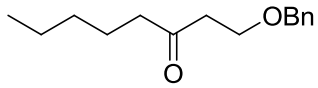
General Procedure 1 for Wacker-oxidation of alkenes (Table 1, Scheme 2, 3, 4 and 5): Palladium acetate (11.5 mg, 0.05 mmol, 5 mol%) and benzoquinone (108 mg, 1.00 mmol) were charged in a resealable 20-mL vial under air. A mixture of MeCN (4.5 mL) and water (0.63 mL) was added, followed by the addition of aqueous HBF_4 (0.18 mL, 48% in water, 1.38 mmol). After the addition of the corresponding substrate (1.00 mmol), the homogenous reaction mixture was stirred for 16 h at room temperature. The crude reaction mixture was then diluted with brine (30 mL) and extracted with CH_2Cl_2 (3x30 mL). The combined organic phases were then dried over Na_2SO_4, filtered, and evaporated in vacuo. NMR-analysis of the

crude mixture was performed to determine the regioselectivity of the process. The crude product was then further purified by column chromatography on silica gel using pentane/ether as eluent.

General Procedure 2 for cross-metathesis reactions using catalyst 1 (Scheme 2 and 4): The corresponding limiting alkene substrate (1 mmol, 1 equiv.) and the excess cross-partner (5.00 mmol, 5 equiv.) were charged in a resealable 20-mL vial in a nitrogen filled drybox. Dry CH_2Cl_2 (2.5 mL) was added, followed by the addition of Grubbs-Hoveyda second generation catalyst (31.3 mg, 0.05 mmol, 5 mol%). The vial was sealed and taken out of the glove-box, put under an Argon atmosphere (balloon) and was stirred for 20 h at 40°C before being quenched by addition of ethyl vinyl ether (few drops). The solvent was then evaporated and the *E*/*Z* ratio was determined by NMR-analysis of the crude reaction mixture. The crude product was then further purified by column chromatography on silica gel using pentane/ether as eluent.

General Procedure 3 for Z-selective cross-metathesis reactions using catalyst 2 (Scheme 3): The corresponding limiting alkene substrate (0.4 mmol) was weighted out in a 4-mL scintillation vial in a nitrogen-filled glove-box. Distilled decene (0.4 mL, 2.1 mmol, 5 equiv) was added, followed by addition of a stock solution of catalyst **2** in THF (0.01 M, 0.8 mL, 0.008 mmol, 2 mol%). The mixture was then stirred open in the glove box for 10 h at the indicated temperature, and was then taken out of the box and quenched by addition of ethyl vinyl ether (few drops). The solvent was evaporated and the *E*/*Z* ratio was determined by NMR-analysis of the crude reaction mixture. The crude product was then further purified by column chromatography on silica gel using pentane/ether as eluent.

1-(benzyloxy)octan-3-one (Table 1, Entry 1)

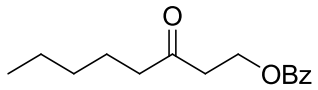


Was obtained in 71% yield (100 mg, 0.43 mmol) following general procedure 1 on a 0.6 mmol scale.

^{1}H NMR (500 MHz, Chloroform-d): δ 7.42–7.19 (m, 5H), 4.51 (s, 2H), 3.74 (t, *J* = 6.3 Hz, 2H), 2.69 (t, *J* = 6.3 Hz, 2H), 2.43 (t, *J* = 7.4 Hz, 2H), 1.58 (p, *J* = 7.2 Hz, 2H), 1.39 – 1.18 (m, 4H), 0.88 (t, *J* = 7.0 Hz, 3H).

Values are in accordance with literature.[1]

3-oxooctyl benzoate (Table 1, Entry 2)



Was obtained in 80% yield (199 mg, 0.80 mmol) following general procedure 1 on a 1 mmol scale.

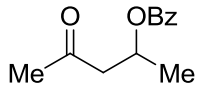
^{1}H NMR (500 MHz, Chloroform-d): δ 8.03–7.96 (m, 2H), 7.58–7.52 (m, 1H), 7.43 (t, *J* = 8.1 Hz, 2H), 4.59 (t, *J* = 6.4 Hz, 2H), 2.87 (t, *J* = 6.4 Hz, 2H), 2.47 (t, *J* = 7.4 Hz, 2H), 1.61 (p, *J* = 7.5 Hz, 2H), 1.35 – 1.21 (m, 4H), 0.88 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, Chloroform-d): δ 208.1, 166.4, 133.0, 123.0, 129.6, 128.3, 60.0, 43.3, 41.4, 31.3, 23.3, 22.4, 13.9.

HRMS (EI): calcd for $C_{15}H_{21}O_3$ (M^+ + H): 249.1491; found 249.1484.

4-oxopentan-2-yl benzoate (Table 1, Entry 3)

[1] *Tetrahedon. Lett* **52**, 2950.

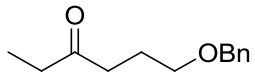


Was obtained in 80% yield (164 mg, 0.80 mmol) following general procedure 1 on a 1 mmol scale.

^{1}H NMR (500 MHz, Chloroform-d): δ 7.99 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.56–7.50 (m, 1H), 7.44–7.39 (m, 2H), 5.53 (h, *J* = 6.3 Hz, 1H), 2.95 (dd, *J* = 16.3, 6.9 Hz, 1H), 2.69 (dd, *J* = 16.3, 6.0 Hz, 1H), 2.18 (s, 3H), 1.40 (d, *J* = 6.3 Hz, 3H).

Values are in accordance with literature.[2]

6-(benzyloxy)hexan-3-one (Table 1, Entry 4)



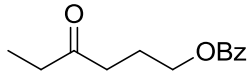
Was obtained in 80% yield (33 mg, 0.16 mmol, 9:1 mixture of regioisomers) following general procedure 1 on a 0.2 mmol scale. The isomers ratio was 6.5:1 in the crude reaction mixture as determined by ^{1}H-NMR.

^{1}H NMR (500 MHz, Chloroform-d, major): δ 7.31 (m, 5H), 4.48 (s, 2H), 3.48 (t, *J* = 6.1 Hz, 2H), 2.52 (t, *J* = 7.2 Hz, 2H), 2.42 (q, *J* = 7.3 Hz, 2H), 1.90 (p, *J* = 6.7 Hz, 2H), 1.04 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (125 MHz, Chloroform-d, major): δ 211.4, 138.4, 128.4, 127.6, 127.6, 72.8, 69.4, 38.9, 36.0, 23.9, 7.8

HRMS (FAB): calcd for $C_{13}H_{19}O_2$ (M^+ + H): 207.1385; found 207.1387.

4-oxohexyl benzoate (Table 1, Entry 5)



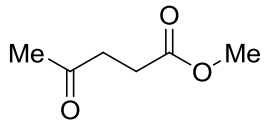
[2] *Tetrahedron Lett*. *49*, 3326.

Was obtained in 83% yield (110 mg, 0.50 mmol, 10:1 mixture of regioisomers) following general procedure 1 on a 0.6 mmol scale.

^{1}H NMR (500 MHz, Chloroform-d): δ 8.03 (d, *J* = 3.0 Hz, 2H), 7.59–7.54 (m, 1H), 7.48–7.42 (m, 2H), 4.33 (t, *J* = 6.4 Hz, 2H), 2.58 (t, *J* = 7.2 Hz, 2H), 2.45 (q, *J* = 7.3 Hz, 2H), 2.12–2.02 (m, 2H), 1.06 (t, *J* = 7.3 Hz, 3H).

Values are in accordance with literature.[3]

methyl 4-oxopentanoate (Table 1, Entry 6)

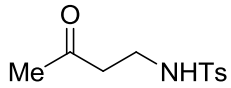


Was obtained in 70% yield (91 mg, 0.7 mmol) following general procedure 1 on a 1 mmol scale.

^{1}H NMR (500 MHz, Chloroform-d): δ 3.64 (s, 3H), 2.73 (t, *J* = 6.6 Hz, 2H), 2.54 (t, *J* = 6.6 Hz, 2H), 2.16 (s, 3H).

Values are in accordance with literature.[4]

4-methyl-N-(3-oxobutyl)benzenesulfonamide (Table 1, Entry 7)



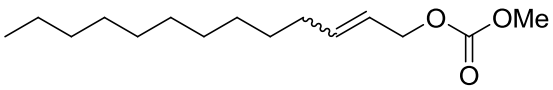
Was obtained in 72% yield (173 mg, 0.72 mmol) following general procedure 1 on a 1 mmol scale.

[3] *Org. Lett. 13*, 4308.
[4] *Org. Lett. 13*, 3856.

^{1}H NMR (500 MHz, Chloroform-d): δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.6 Hz, 2H), 5.22 (t, *J* = 6.5 Hz, 1H), 3.14 – 3.08 (m, 2H), 2.67 (t, *J* = 5.8 Hz, 2H), 2.41 (s, 3H), 2.09 (s, 3H).

Values are in accordance with literature.[5]

methyl tridec-2-enyl carbonate (Scheme 2)



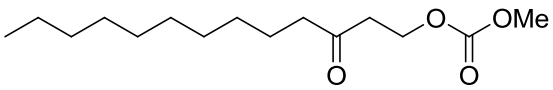
Was obtained in 68% yield (350 mg, 1.37 mmol, 10:1 *E*/*Z*) following general procedure 2 on a 2 mmol scale using dodecene as the limiting alkene and allyl carbonate as the cross-partner (4 equiv).

^{1}H NMR (500 MHz, Chloroform-d, major): δ 5.85–5.76 (m, 1H), 5.62–5.53 (m, 1H), 4.61–4.52 (m, 2H), 3.78 (s, 3H), 2.05 (q, *J* = 7.0 Hz, 2H), 1.36 (m, 2H), 1.29 (m, 14H), 0.88 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, Chloroform-d, major): δ 155.7, 137.6, 123.0, 68.7, 54.7, 32.2, 31.9, 29.6, 29.6, 29.4, 29.3, 29.1, 28.8, 22.7, 14.1.

HRMS (EI): calcd for $C_{15}H_{28}O_3$ (M^+): 256.2038; found 256.2035.

methyl 3-oxotridecyl carbonate (Scheme 2)



Was obtained in 80% yield (65 mg, 0.24 mmol) following general procedure 1 on a 0.3 mmol scale.

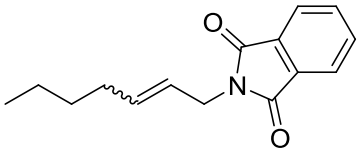
[5] *Tetrahedron 53*, 8887.

^{1}H NMR (500 MHz, Chloroform-d): δ 4.39 (t, *J* = 6.3 Hz, 2H), 3.77 (s, 3H), 2.77 (t, *J* = 6.3 Hz, 2H), 2.47–2.37 (m, 2H), 1.64–1.49 (m, 2H), 1.25 (d, *J* = 7.2 Hz, 14H), 0.87 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, Chloroform-d): δ 207.6, 155.5, 62.8, 54.8, 43.3, 41.2, 31.9, 29.5, 29.4, 29.4, 29.3, 29.1, 23.5, 22.7, 14.1.

HRMS (EI): calcd for $C_{15}H_{29}O_4$ ($M+H^+$): 273.2066; found 273.2067.

2-(hept-2-enyl)isoindoline-1,3-dione (Scheme 2)



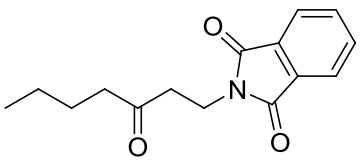
Was obtained in 70% yield (170 mg, 0.70 mmol, 7:1 *E*/*Z*) following general procedure 2 on a 1 mmol scale using allyl phthalimide as the limiting reagent and hexene as the cross-partner (5 equiv).

^{1}H NMR (500 MHz, Chloroform-d, major): δ 7.84 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.70 (dd, *J* = 5.5, 3.0 Hz, 2H), 5.79–5.69 (m, 1H), 5.55–5.43 (m, 1H), 4.23 (dq, *J* = 6.3, 1.0 Hz, 2H), 2.00 (q, *J* = 7.8 Hz, 2H), 1.43–1.18 (m, 4H), 0.86 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (125 MHz, Chloroform-d, major): δ 168.0, 135.3, 133.8, 132.2, 123.2, 123.0, 39.6, 31.8, 31.0, 22.2, 13.9.

HRMS (EI): calcd for $C_{15}H_{17}O_2N$ (M^+): 243.1259; found 243.1265.

2-(3-oxoheptyl)isoindoline-1,3-dione (Scheme 2)



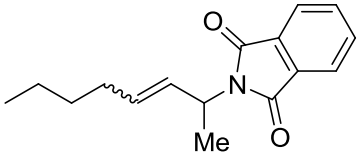
Was obtained in 77% yield (40 mg, 0.15 mmol) following general procedure 1 on a 0.2 mmol scale.

^{1}H NMR (500 MHz, Chloroform-d): δ 7.83 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.70 (dd, *J* = 5.5, 3.0 Hz, 2H), 3.99–3.89 (m, 2H), 2.84 (dd, *J* = 7.9, 7.0 Hz, 2H), 2.46–2.38 (m, 2H), 1.59–1.51 (m, 2H), 1.34–1.25 (m, 2H), 0.88 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (125 MHz, Chloroform-d): δ 208.2, 168.1, 134.0, 132.0, 123.2, 42.6, 40.5, 33.0, 25.7, 22.3, 13.8.

HRMS (EI): calcd for $C_{15}H_{17}O_3N$ (M^+): 259.1208; found 259.1209.

2-(oct-3-en-2-yl)isoindoline-1,3-dione (Scheme 2)



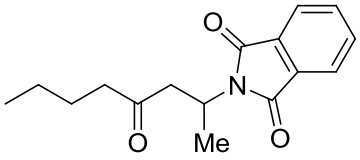
Was obtained in 78% yield (100 mg, 0.39 mmol, 10:1 *E*/*Z*) following general procedure 2 on a 0.5 mmol scale using 2-butenylphthalimide as the limiting reagent and hexene as the cross-partner (5 equiv).

^{1}H NMR (500 MHz, Chloroform-d, major): δ 7.81 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.69 (dd, *J* = 5.5, 3.0 Hz, 2H), 5.87 (ddt, *J* = 15.4, 7.6, 1.5 Hz, 1H), 5.67 (dtd, *J* = 15.4, 6.7, 1.1 Hz, 1H), 4.93–4.84 (m, 1H), 2.06–1.97 (m, 2H), 1.55 (d, *J* = 7.1 Hz, 3H), 1.36–1.25 (m, 4H), 0.87 (t, *J* = 7.4, 3H).

^{13}C NMR (125 MHz, Chloroform-d, major): δ 168.0, 133.8, 133.3, 132.1, 128.4, 123.0, 48.9, 31.8, 31.1, 22.2, 19.0, 13.9.

HRMS (EI): calcd for $C_{16}H_{19}O_2N$ (M^+): 257.1416; found 257.1415.

2-(4-oxooctan-2-yl)isoindoline-1,3-dione (Scheme 2)



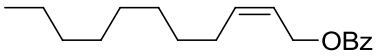
Was obtained in 75% yield (30.6 mg, 0.11 mmol) following general procedure 1 on a 0.15 mmol scale. A single isomer was observed by crude NMR-analysis, accompanied by a small impurity that was not assigned to the minor regioisomer.

^{1}H NMR (500 MHz, Chloroform-d, major): δ 7.80 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.69 (dd, *J* = 5.5, 3.0 Hz, 2H), 4.90–4.78 (m, 1H), 3.27 (dd, *J* = 17.6, 8.1 Hz, 1H), 2.96 (dd, *J* = 17.6, 6.4 Hz, 1H), 2.39 (td, *J* = 7.5, 3.7 Hz, 2H), 1.54–1.47 (m, 2H), 1.43 (d, *J* = 6.9 Hz, 3H), 1.30–1.22 (m, 2H), 0.85 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (125 MHz, Chloroform-d, major): δ 208.3, 168.2, 133.8, 131.9, 123.1, 45.7, 42.8, 42.5, 25.7, 22.2, 18.9, 13.8.

HRMS (EI): calcd for $C_{16}H_{19}O_3N$ (M^+): 273.1365; found 273.1366.

(Z)-undec-2-enyl benzoate (Scheme 3)



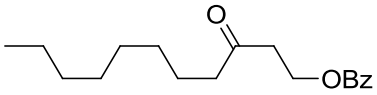
Was obtained in 71% yield (78 mg, 0.29 mmol, > 95% *Z*) following general procedure 3 at 35 °C on a 0.4 mmol scale using allyl benzoate as the limiting reagent.

^{1}H NMR (500 MHz, Chloroform-d): δ 8.05 (dd, *J* = 7.9, 1.7 Hz, 2H), 7.59 – 7.52 (m, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 5.69 (tq, *J* = 11.2, 6.1, 5.1 Hz, 2H), 4.87 (d, *J* = 6.2 Hz, 2H), 2.17 (q, *J* = 7.1 Hz, 2H), 1.39 (q, *J* = 7.3 Hz, 2H), 1.35–1.18 (m, 10H), 0.87 (t, *J* = 6.7 Hz, 3H).

^{13}C NMR (125 MHz, Chloroform-d): δ 166.6, 135.8, 132.9, 130.3, 129.6, 128.3, 123.2, 60.9, 31.9, 29.4, 29.4, 29.3, 29.2, 27.6, 22.7, 14.1.

HRMS (FAB): calcd for $C_{18}H_{27}O_2$ (M^+ +H): 275.2011; found 275.2007.

3-oxoundecyl benzoate (Scheme 3)



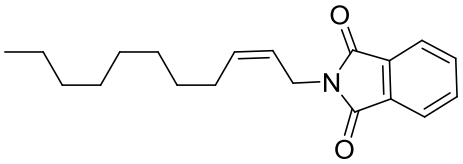
Was obtained in 71% yield (41 mg, 0.14 mmol) following general procedure 1 on a 0.2 mmol scale.

^{1}H NMR (500 MHz, Chloroform-d, major): δ 7.99 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.57–7.52 (m, 1H), 7.45–7.39 (m, 2H), 4.59 (t, *J* = 6.3 Hz, 2H), 2.87 (t, *J* = 6.3 Hz, 2H), 2.46 (t, *J* = 7.4 Hz, 2H), 1.59 (m, 2H), 1.31–1.22 (m, 10H), 0.87 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (125 MHz, Chloroform-d, major): δ 208.1, 166.4, 133.0, 129.6, 128.3, 128.3, 60.0, 43.3, 41.4, 31.8, 29.3, 29.2, 29.1, 23.7, 22.6, 14.1.

HRMS (FAB): calcd for $C_{18}H_{27}O_3$ (M^+ +H): 291.1960; found 291.1956.

(Z)-2-(undec-2-enyl)isoindoline-1,3-dione (Scheme 3)



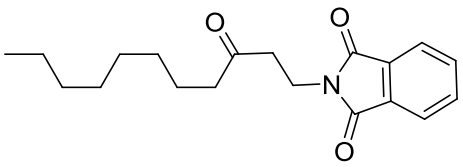
Was obtained in 62% yield (74 mg, 0.25 mmol, >95% *Z*) following general procedure 3 at RT on a 0.4 mmol scale using allyl phthalimide as the limiting reagent.

^{1}H NMR (500 MHz, Chloroform-d, major): δ 7.84 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.70 (dd, *J* = 5.5, 3.0 Hz, 2H), 5.59 (dtt, *J* = 10.4, 7.4, 1.4 Hz, 1H), 5.50–5.42 (m, 1H), 4.31 (ddt, *J* = 7.0, 1.4, 0.6 Hz, 2H), 2.25 (qd, *J* = 7.4, 1.6 Hz, 2H), 1.44–1.36 (m, 2H), 1.36–1.21 (m, 10H), 0.91–0.85 (m, 3H).

^{13}C NMR (125 MHz, Chloroform-d, major): δ 168.0, 134.7, 133.9, 132.2, 123.2, 122.7, 34.9, 31.9, 29.5, 29.4, 29.3, 29.3, 27.4, 22.7, 14.1.

HRMS (EI): calcd for $C_{19}H_{25}O_2N$ (M^+): 299.1885; found 299.1890.

2-(3-oxoundecyl)isoindoline-1,3-dione (Scheme 3)



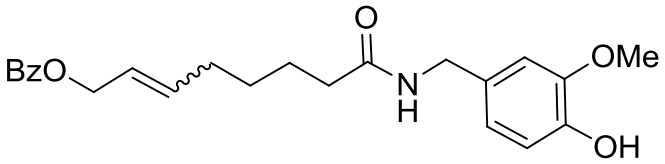
Was obtained in 79% yield (25 mg, 0.08 mmol) following general procedure 3 on a 0.1 mmol scale.

^{1}H NMR (500 MHz, Chloroform-d): δ 7.83 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.71 (dd, *J* = 5.5, 3.0 Hz, 2H), 3.97–3.93 (m, 2H), 2.84 (dd, *J* = 7.9, 7.0 Hz, 2H), 2.42 (t, *J* = 7.5 Hz, 2H), 1.60–1.50 (m, 2H), 1.31–1.20 (m, 10H), 0.89–0.84 (m, 3H).

^{13}C NMR (125 MHz, Chloroform-d): δ 208.3, 168.1, 134.0, 132.0, 123.3, 42.9, 40.5, 33.0, 31.8, 29.3, 29.2, 29.1, 23.6, 22.6, 14.1.

HRMS (EI): calcd for $C_{19}H_{25}O_3N$ (M^+): 315.1834; found 315.1822.

8-(4-hydroxy-3-methoxybenzylamino)-8-oxooct-2-enyl benzoate (Scheme 4)



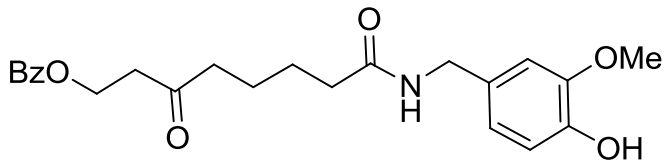
Was obtained in 64% yield (84 mg, 0.21 mmol, *E*/*Z* 6:1) following general procedure 2 on a 0.33 mmol scale using capsaicin as limiting reagent and *cis*-dibenzoylbutenol (5 equiv) as cross-partner.

^{1}H NMR (500 MHz, Chloroform-d, major): δ 8.07–8.02 (m, 2H), 7.59–7.52 (m, 1H), 7.46–7.39 (m, 2H), 6.86 (d, *J* = 8.0 Hz, 1H), 6.81–6.74 (m, 2H), 5.86–5.79 (m, 1H), 5.73–5.61 (m, 3H), 4.75 (dq, *J* = 6.3, 1.0 Hz, 2H), 4.35 (d, *J* = 5.6 Hz, 2H), 3.86 (s, 3H), 2.21 (t, *J* = 7.6 Hz, 2H), 2.14–2.07 (m, 2H), 1.75–1.58 (m, 2H), 1.45 (tdd, *J* = 9.9, 7.2, 5.6 Hz, 2H).

^{13}C NMR (125 MHz, Chloroform-d, major): δ 172.6, 166.4, 146.7, 145.1, 135.8, 132.9, 130.3, 130.3, 129.6, 128.3, 124.3, 120.8, 114.3, 110.7, 65.6, 55.9, 43.5, 36.6, 32.0, 28.4, 25.2.

HRMS (FAB): calcd for $C_{23}H_{28}O_5N$ (M^+): 398.1967; found 398.1966.

8-(4-hydroxy-3-methoxybenzylamino)-3,8-dioxooctyl benzoate (Scheme 4)



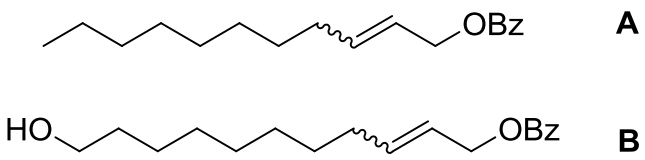
Was obtained in 78% yield (32 mg, 0.08 mmol, 20:1 mixture of isomers) following general procedure 1 on a 0.1 mmol scale.

^{1}H NMR (500 MHz, Chloroform-d, major): δ 8.01–7.95 (m, 2H), 7.54 (ddt, *J* = 7.9, 7.0, 1.3 Hz, 1H), 7.45–7.38 (m, 2H), 6.85 (d, *J* = 8.0 Hz, 1H), 6.79 (d, *J* = 1.9 Hz, 1H), 6.75 (dd, *J* = 8.1, 2.0 Hz, 1H), 5.86 (t, *J* = 5.5 Hz, 1H), 5.70 (s, 1H), 4.57 (t, *J* = 6.3 Hz, 2H), 4.33 (d, *J* = 5.6 Hz, 2H), 3.86 (s, 3H), 2.85 (t, *J* = 6.3 Hz, 2H), 2.51 (t, *J* = 6.6 Hz, 2H), 2.27–2.16 (m, 2H), 1.65 (m, 4H).

^{13}C NMR (125 MHz, Chloroform-d, major): δ 207.6, 172.3, 166.4, 146.7, 145.1, 133.1, 130.2, 129.9, 129.5, 128.4, 120.8, 114.4, 110.7, 59.9, 55.9, 43.6, 42.8, 41.5, 36.4, 25.0, 23.0.

HRMS (FAB): calcd for $C_{23}H_{28}O_6N$ (M^+): 414.1917; found 414.1928.

(*E*)-undec-2-enyl benzoate (A) and (*E*)-11-hydroxyundec-2-enyl benzoate (B) (Scheme 4)



A and B were obtained in 62% yield (170 mg, 0.62 mmol, *E*/*Z* 7:1, **A**) and 63% yield (182 mg, 0.63 mmol, *E*/*Z* 8:1, **B**) following general procedure 2 on a 1 mmol scale using oleyl alcohol as limiting reagent and *cis*-dibenzoylbutenol (5 equiv) as cross-partner.

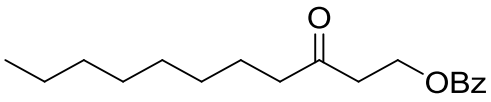
A: see below

B: ^{1}H NMR (500 MHz, Chloroform-d, major): δ 8.09–8.02 (m, 2H), 7.58–7.53 (m, 1H), 7.46–7.41 (m, 2H), 5.91–5.80 (m, 1H), 5.73–5.63 (m, 1H), 4.77 (dq, *J* = 6.4, 1.0 Hz, 2H), 3.64 (t, *J* = 6.6 Hz, 2H), 2.11–2.05 (m, 2H), 1.61–1.25 (m, 13H).

^{13}C NMR (125 MHz, Chloroform-d, major): δ 166.5, 136.6, 132.9, 130.4, 129.6, 128.3, 123.8, 65.8, 63.1, 32.8, 32.3, 29.4, 29.3, 29.1, 28.8, 25.7.

HRMS (FAB): calcd for $C_{18}H_{27}O_3$ (M^+ + H): 291.1960; found 291.1965.

3-oxoundecyl benzoate (Scheme 4)



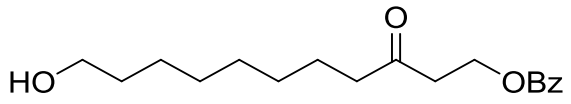
Was obtained in 78% yield (45 mg, 0.16 mmol) following general procedure 1 on a 0.2 mmol scale. Isomeric ratio was 20:1 by NMR-analysis of the crude.

^{1}H NMR (500 MHz, Chloroform-d): δ 7.99 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.58–7.52 (m, 1H), 7.46–7.38 (m, 2H), 4.59 (t, *J* = 6.3 Hz, 2H), 2.87 (t, *J* = 6.3 Hz, 2H), 2.46 (t, *J* = 7.4 Hz, 2H), 1.60 (t, *J* = 7.3 Hz, 2H), 1.32 – 1.18 (m, 10H), 0.87 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (125 MHz, Chloroform-d): δ 208.1, 166.4, 133.0, 129.6, 128.3, 128.3, 60.0, 43.3, 41.4, 31.8, 29.3, 29.2, 29.1, 23.7, 22.6, 14.1.

HRMS (FAB): calcd for $C_{18}H_{27}O_3$ (M^++H): 291.1960; found 291.1956.

11-hydroxy-3-oxoundecyl benzoate (Scheme 4)



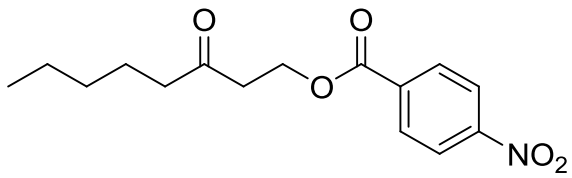
Was obtained in 77% yield (47 mg, 0.15 mmol, *E*/*Z* 6:1) following general procedure 1 on a 0.2 mmol scale.

^{1}H NMR (500 MHz, Chloroform-d): 8.01–7.96 (m, 2H), 7.57–7.52 (m, 1H), 7.44–7.39 (m, 2H), 4.58 (t, *J* = 6.3 Hz, 2H), 3.62 (t, *J* = 6.6 Hz, 2H), 2.86 (t, *J* = 6.3 Hz, 2H), 2.46 (t, *J* = 7.4 Hz, 2H), 1.64–1.49 (m, 3H), 1.36–1.24 (m, 10H).

^{13}C NMR (125 MHz, Chloroform-d): δ 208.1, 166.4, 133.0, 123.0, 129.6, 128.3, 63.0, 60.0, 43.2, 41.4, 32.7, 29.3, 29.2, 29.0, 25.6, 23.6.

HRMS (FAB): calcd for $C_{18}H_{27}O_4$ (M^++H): 307.1909; found 307.1919.

3-oxooctyl 4-nitrobenzoate (Scheme 5)



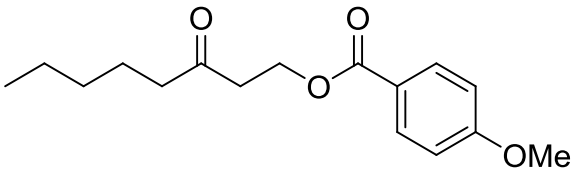
Was obtained in 76% yield (133 mg, 0.45 mmol) following general procedure 1 on a 0.6 mmol scale. Isomeric ratio was 28:1 as determined by NMR analysis of the crude reaction mixture.

^{1}H NMR (500 MHz, Chloroform-d): δ 8.26 (d, *J* = 8.8 Hz, 2H), 8.15 (d, *J* = 8.9 Hz, 2H), 4.63 (t, *J* = 6.2 Hz, 2H), 2.90 (t, *J* = 6.2 Hz, 2H), 2.47 (t, *J* = 7.4 Hz, 2H), 1.65–1.54 (m, 2H), 1.35–1.20 (m, 4H), 0.87 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, Chloroform-d): δ 207.6, 164.5, 150.5, 135.3, 130.7, 123.5, 60.7, 43.2, 41.1, 31.3, 23.3, 22.4, 13.9.

HRMS (EI): calcd for $C_{15}H_{20}O_5N$ (M^++H): 294.1341; found 294.1352.

3-oxooctyl 4-methoxybenzoate (Scheme 5)



Was obtained in 74% yield (124 mg, 0.45 mmol) following general procedure 1 on a 0.6 mmol scale. Isomeric ratio was 16:1 as determined by NMR analysis of the crude reaction mixture.

^{1}H NMR (500 MHz, Chloroform-d, major): δ 7.94 (d, *J* = 8.9 Hz, 2H), 6.89 (d, *J* = 8.9 Hz, 1H), 4.55 (t, *J* = 6.4 Hz, 2H), 3.84 (s, 3H), 2.85 (t, *J* = 6.4 Hz, 2H), 2.45 (t, *J* = 7.4 Hz, 2H), 1.59 (tt, *J* = 8.0, 7.1 Hz, 2H), 1.36–1.20 (m, 5H), 0.87 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, Chloroform-d, major): δ 208.3, 166.1, 163.4, 131.6, 122.4, 113.6, 59.7, 55.4, 43.3, 41.5, 31.3, 23.3, 22.4, 13.9.

HRMS (EI): calcd for $C_{16}H_{22}O_4$ (M^+): 278.1518; found 278.1509.

Intermolecular Competition experiments (Scheme 5)

Three competition experiments were run using 5 mol% catalyst and only 10 mol% benzoquinone to enable only low conversions to be achieved. A 1:1 ratio of competing substrates was used, and after two hours the ratio of products was determined by analysis of the proton NMR. Results:

MeO vs H: **1.2 to 1**

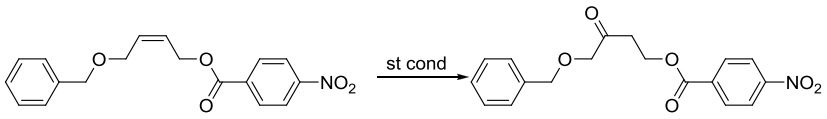
NO_2 vs H: **0.5 to 1**

MeO vs NO_2: **2.4 to 1**

OBz vs OBn **1 to 3.5**

OBn vs CH_2OBz **1 to 2.2** (therefore CH_2OBz is 2.2*3.5 = 7.7 faster than OBz)

Intermolecular Competition experiments (Scheme 5)

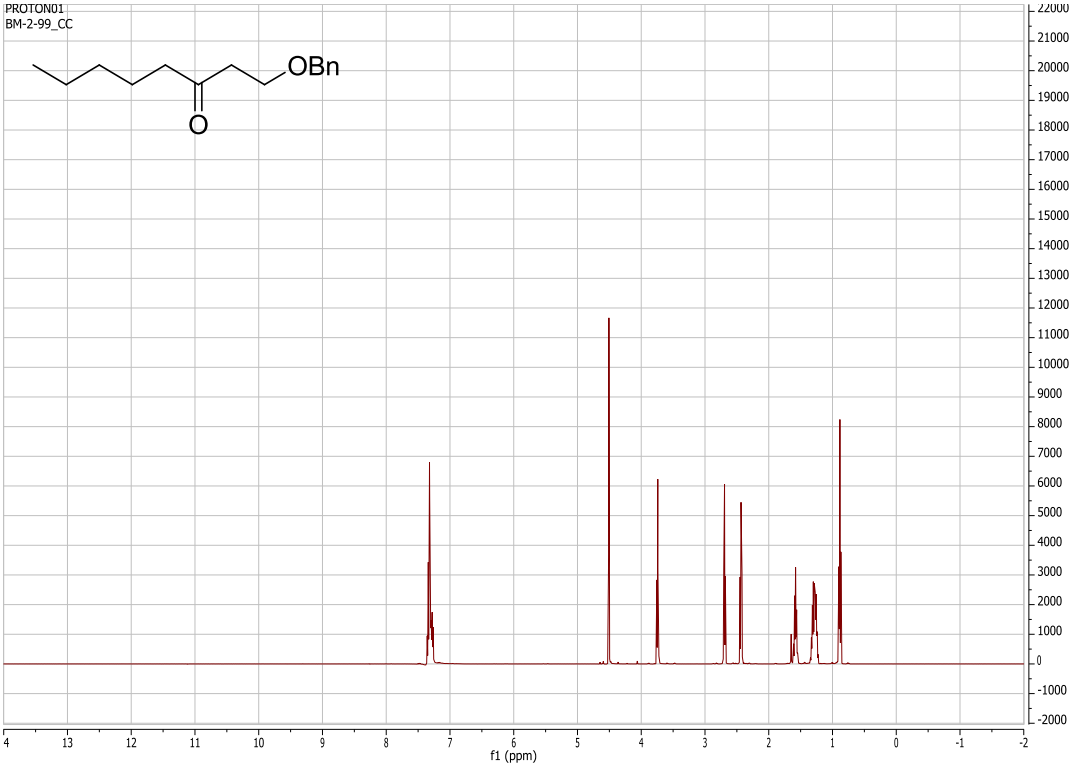


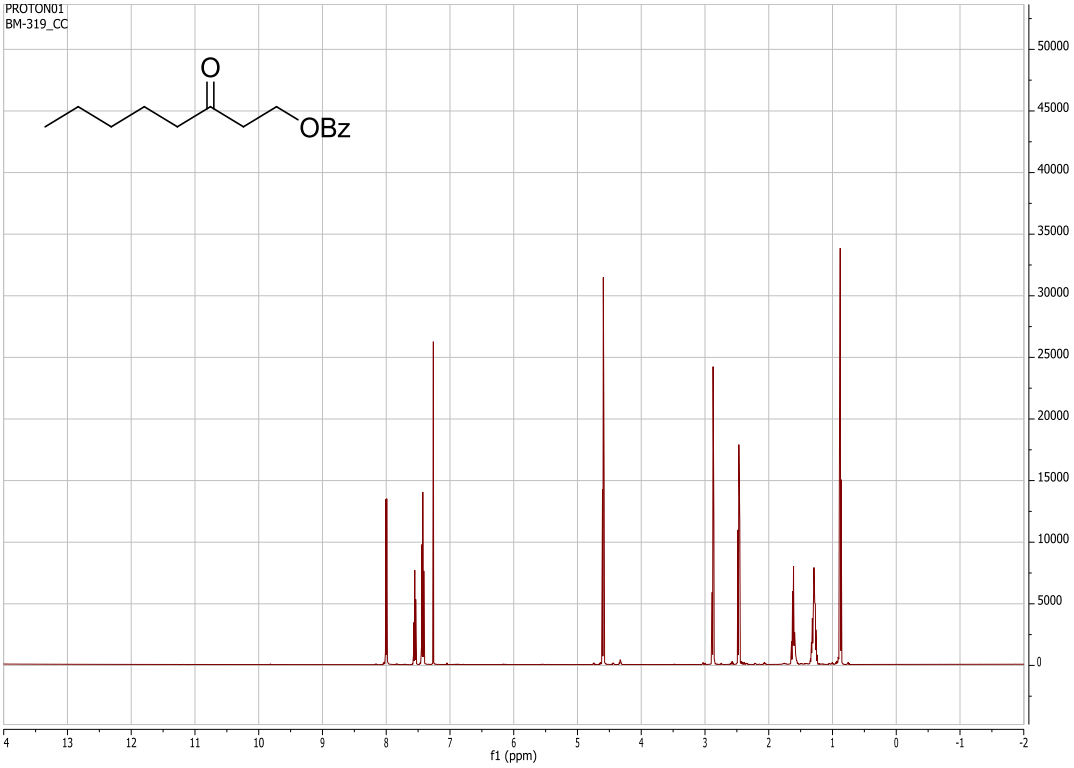
Was obtained in 50% yield (34.3 mg, 0.1 mmol) following general procedure 1 on a 0.2 mmol scale. Isomeric ratio was 31:1 as determined by NMR analysis of the crude reaction mixture. Peaks for the minor and major isomer were assigned by comparison of the triplet shifts in the H-NMR with the compounds made above and matched their values (major, triplet next to 4-NO_2BzO: 4.62; minor, triplet next to OBn: 3.77)

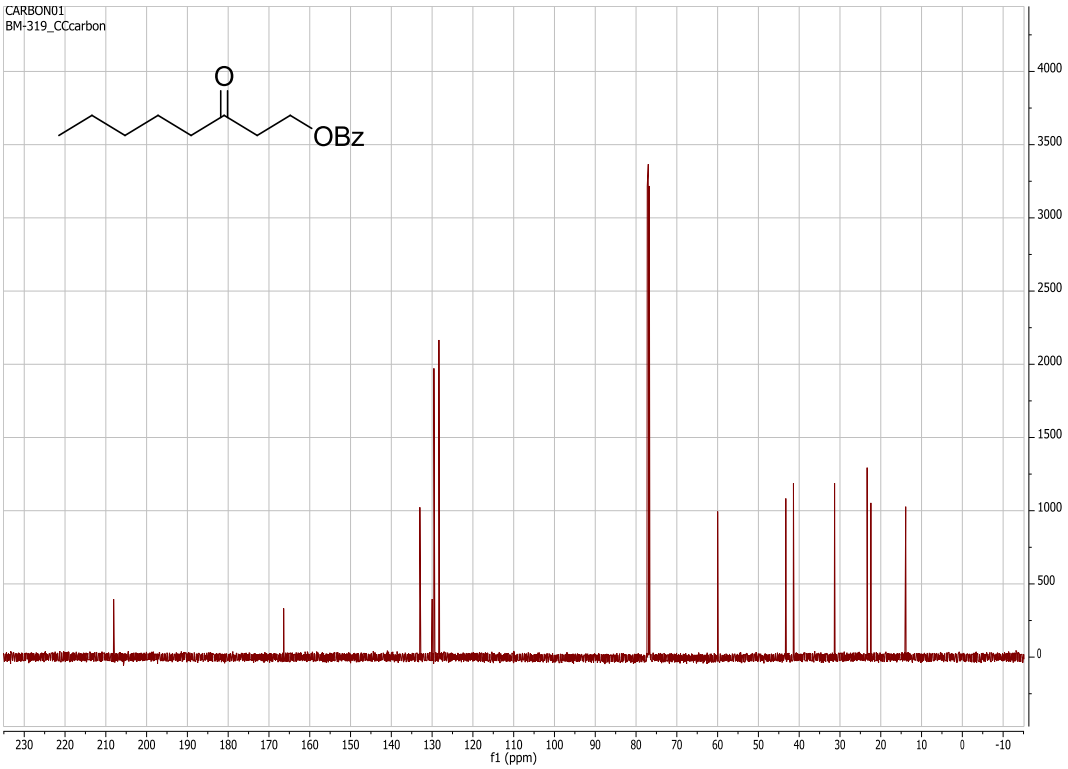
^{1}H NMR (500 MHz, Chloroform-d, major): δ 8.26 (d, *J* = 9.0 Hz, 2H), 8.15 (d, *J* = 9.0 Hz, 2H), 7.39 – 7.32 (m, 5H), 4.66 (t, *J* = 6.2 Hz, 2H), 4.61 (s, 2H), 4.11 (s, 2H), 3.02 (t, *J* = 6.2 Hz, 2H).

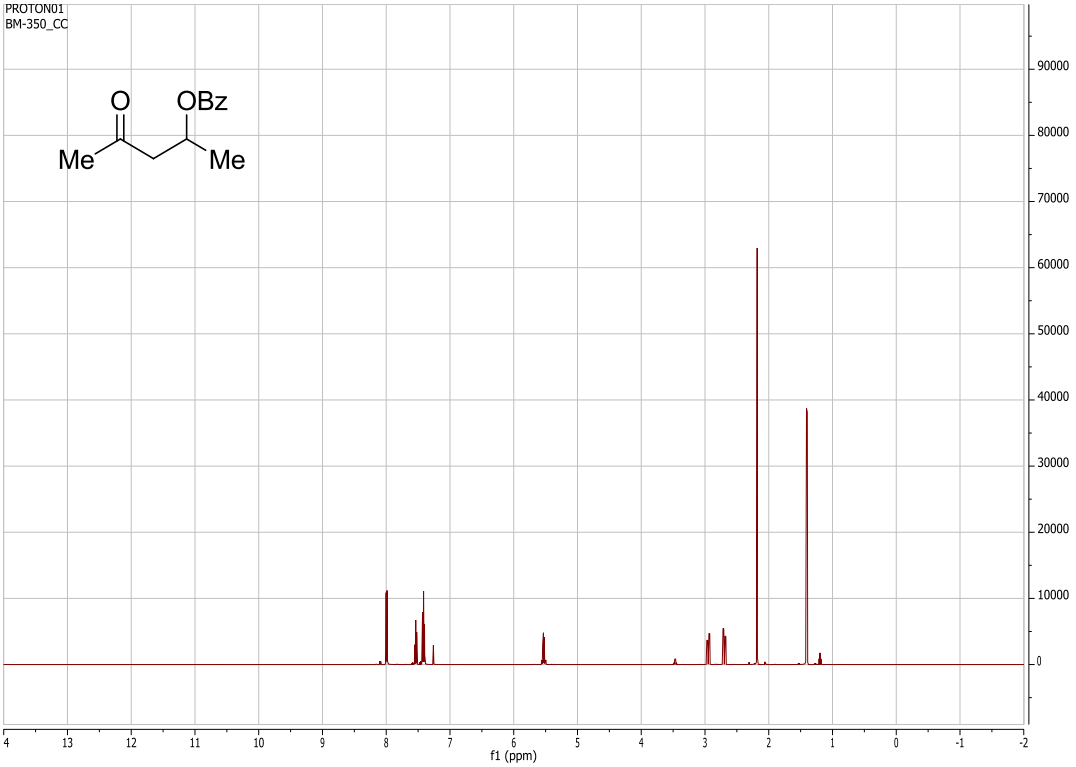
^{13}C NMR (125 MHz, Chloroform-d, major): δ 205.8, 164.5, 150.6, 136.8, 135.3, 130.7, 128.6, 128.2, 127.9, 123.8, 75.2, 73.5, 60.3, 38.0.

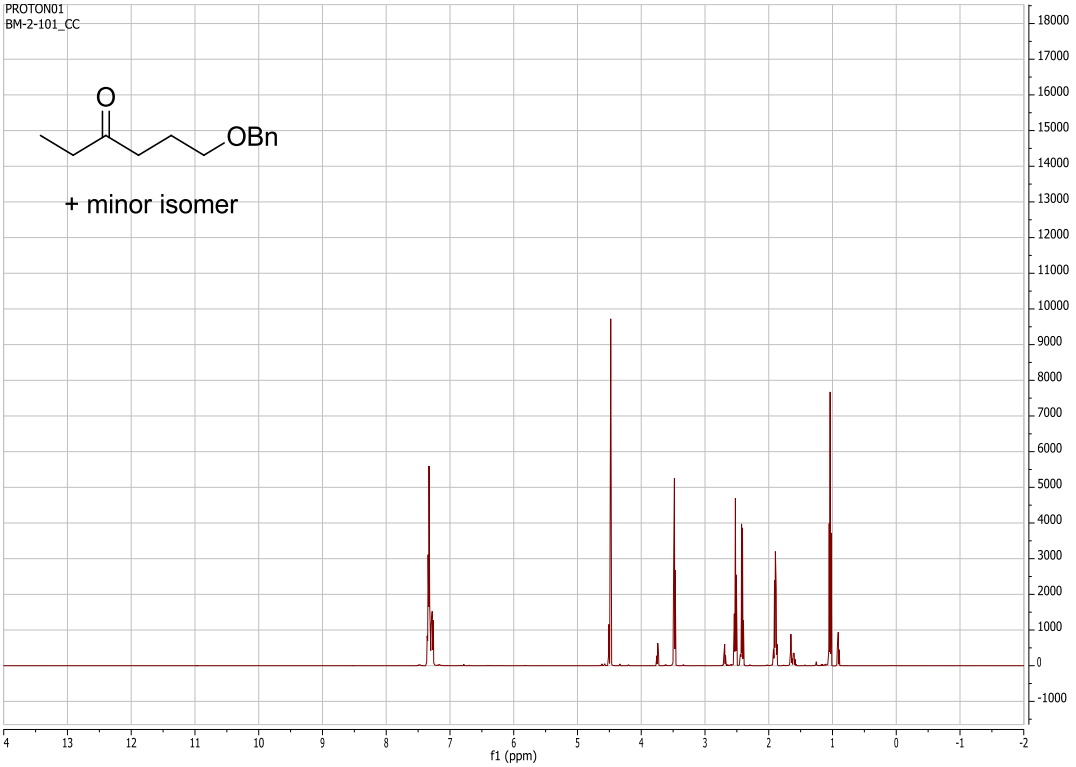
HRMS (EI): calcd for $C_{18}H_{18}NO_6$ ($M+H^+$): 344.1134; found 344.1121.

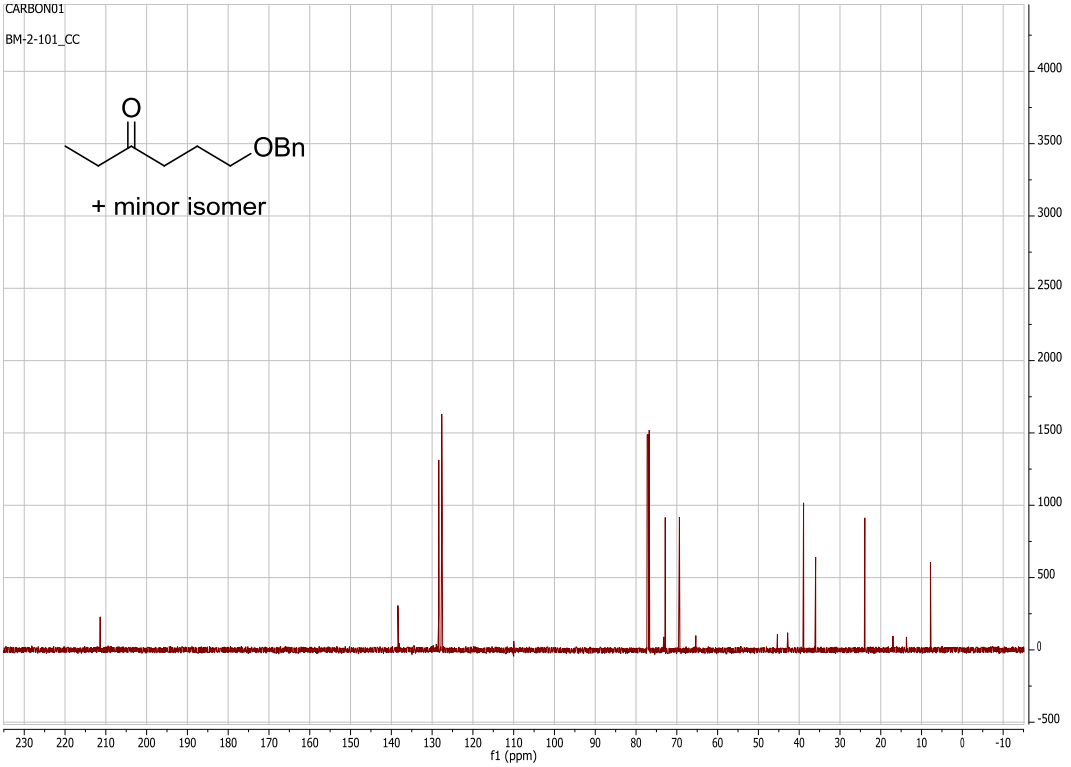

PROTON01
BM-2-99_CC
OBn
O
f1 (ppm)

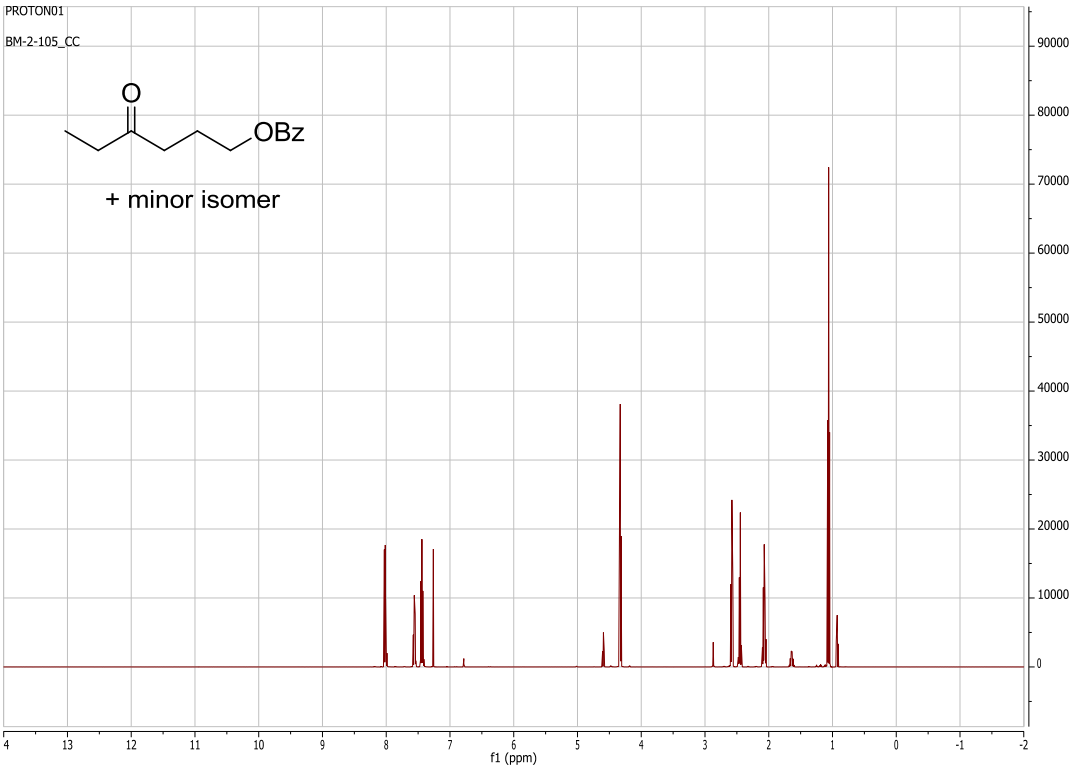

PROTON01
BM-319_CC
O
OBz
f1 (ppm)

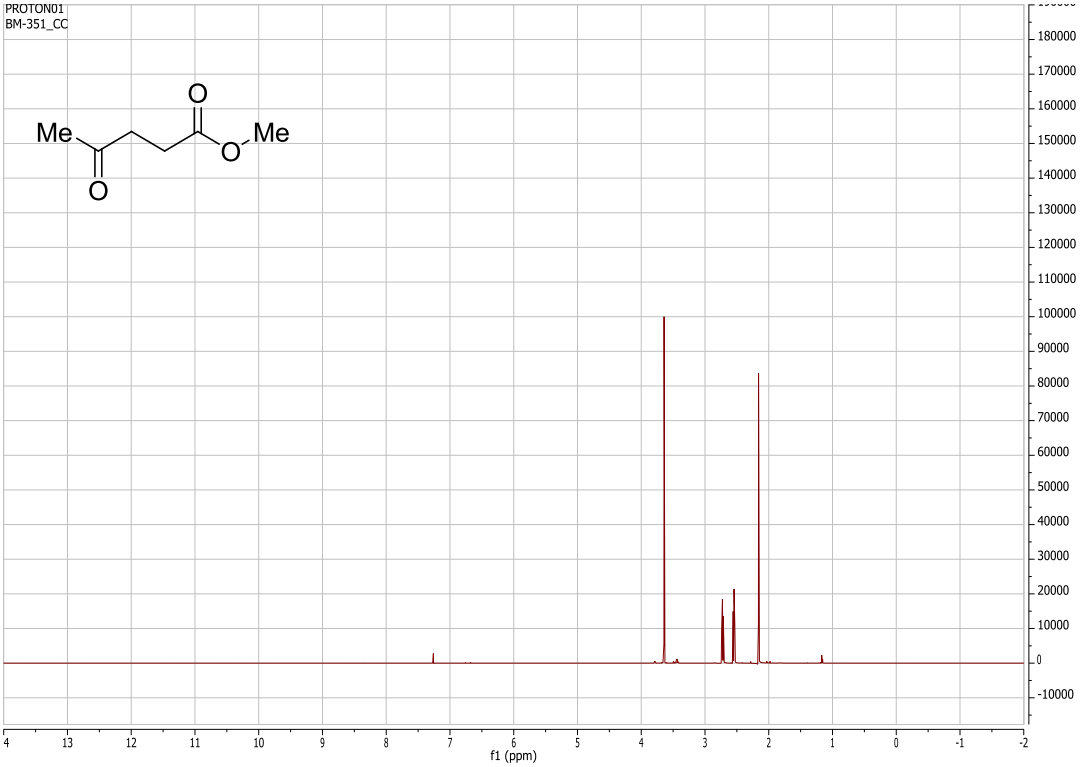

CARBON01
BM-319_CCcarbon
O
OBz
4000
3500
3000
2500
2000
1500
1000
500
0
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

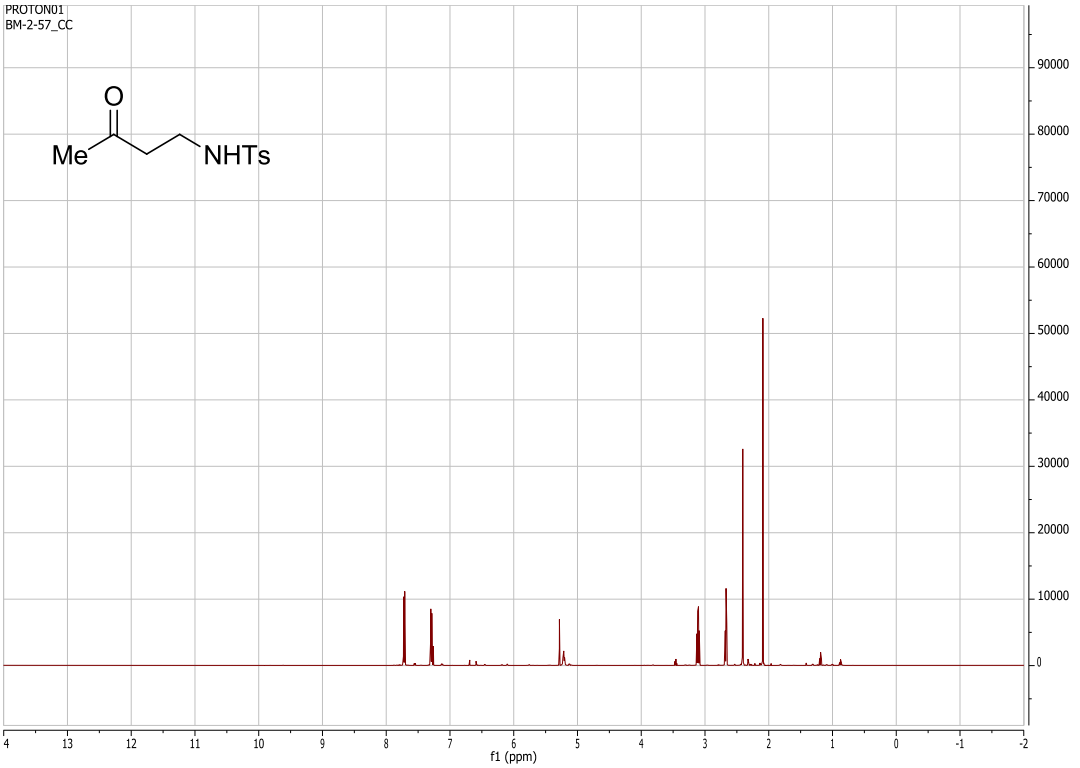

PROTON01
BM-350_CC
O
OBz
Me
Me
f1 (ppm)

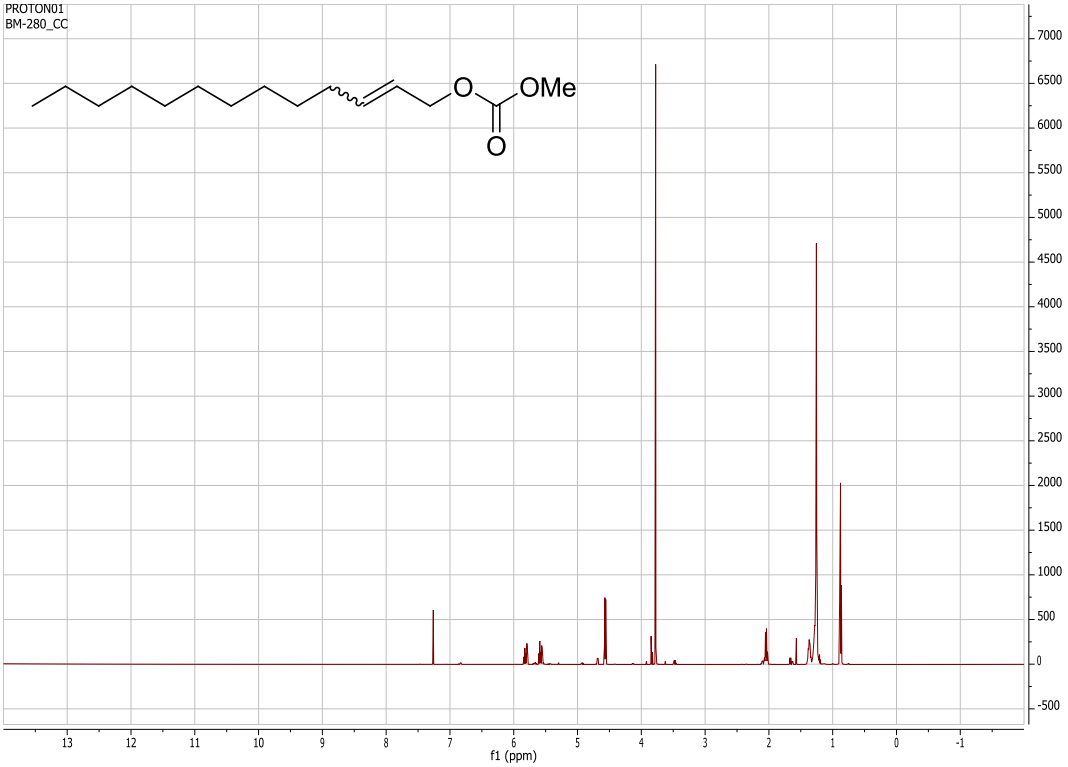

PROTON01
BM-2-101_CC
O
OBn
+ minor isomer
f1 (ppm)

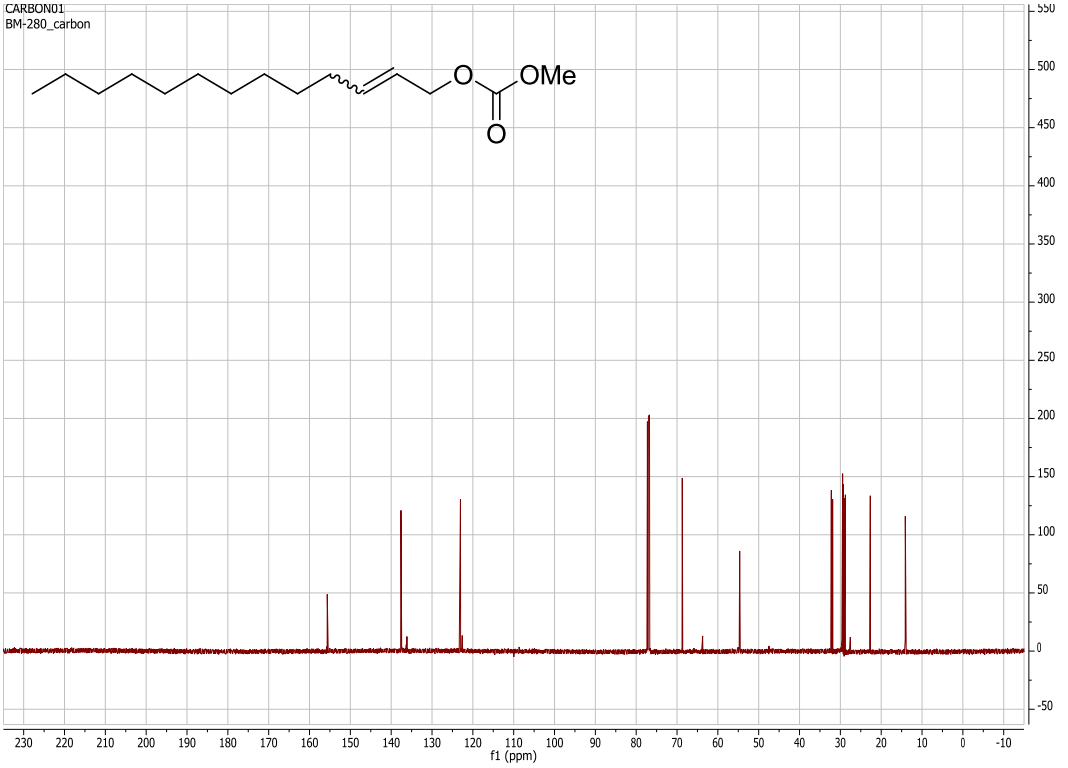

CARBON01
BM-2-101_CC
O
OBn
+ minor isomer
f1 (ppm)

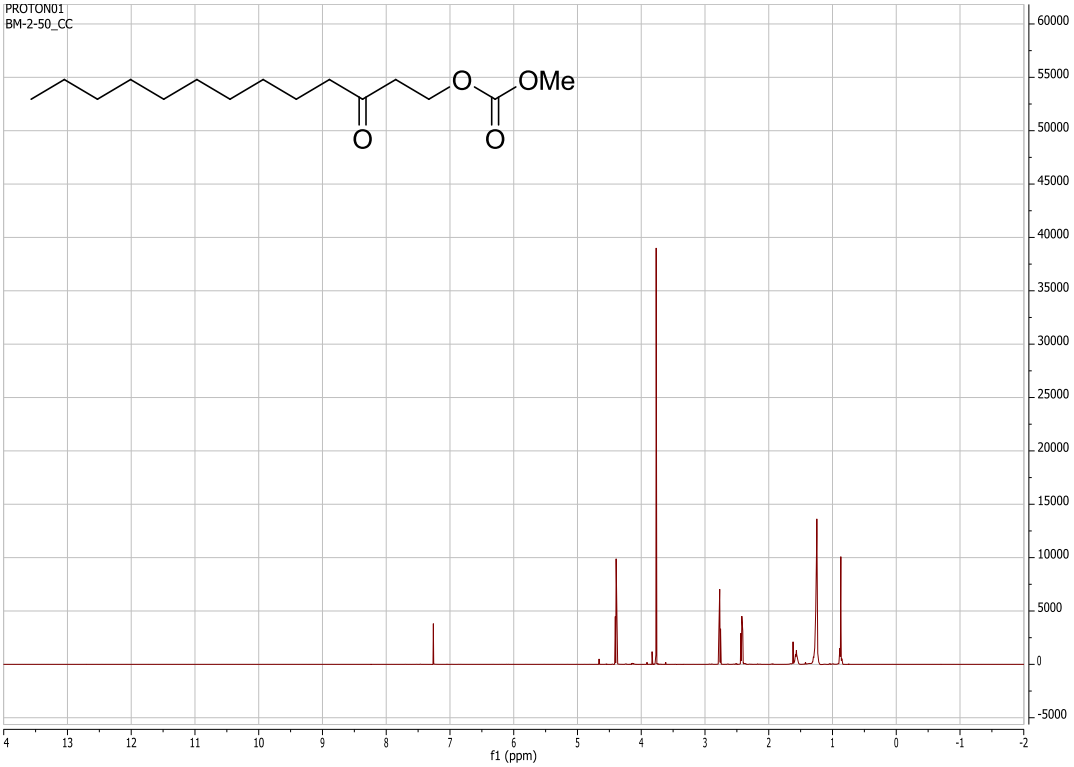

PROTON01
BM-2-105_CC
O
OBz
+ minor isomer
f1 (ppm)

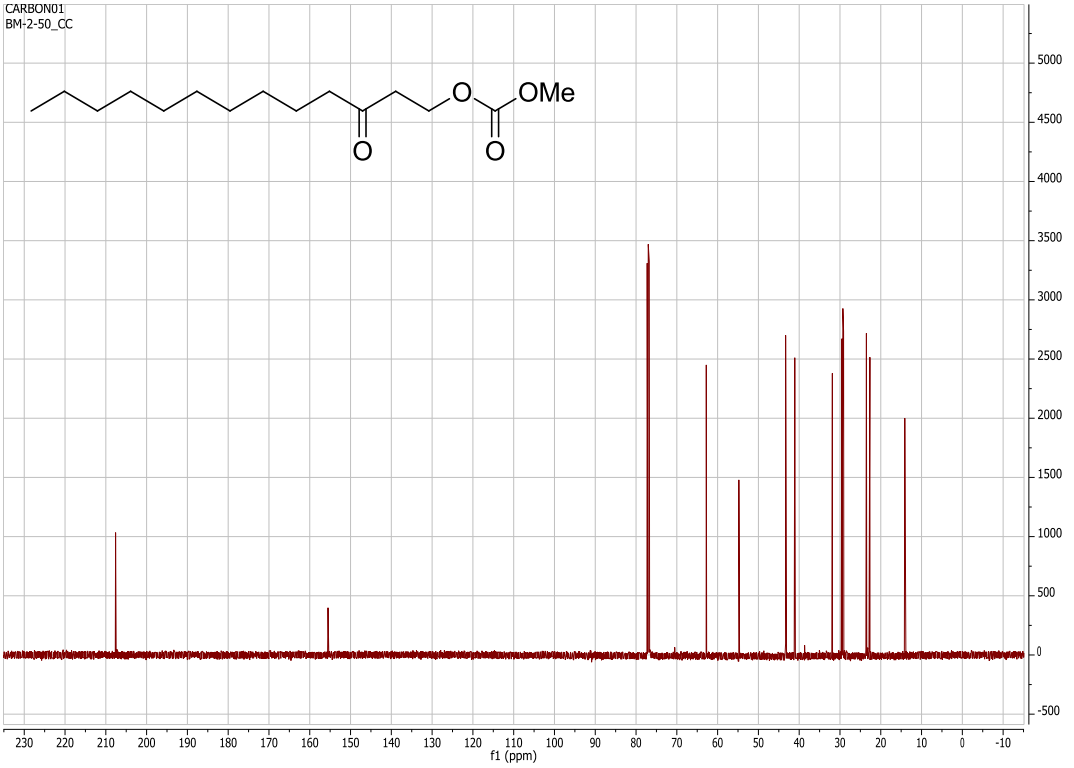

PROTON01
BM-351_CC
Me
O
O
O
Me
f1 (ppm)

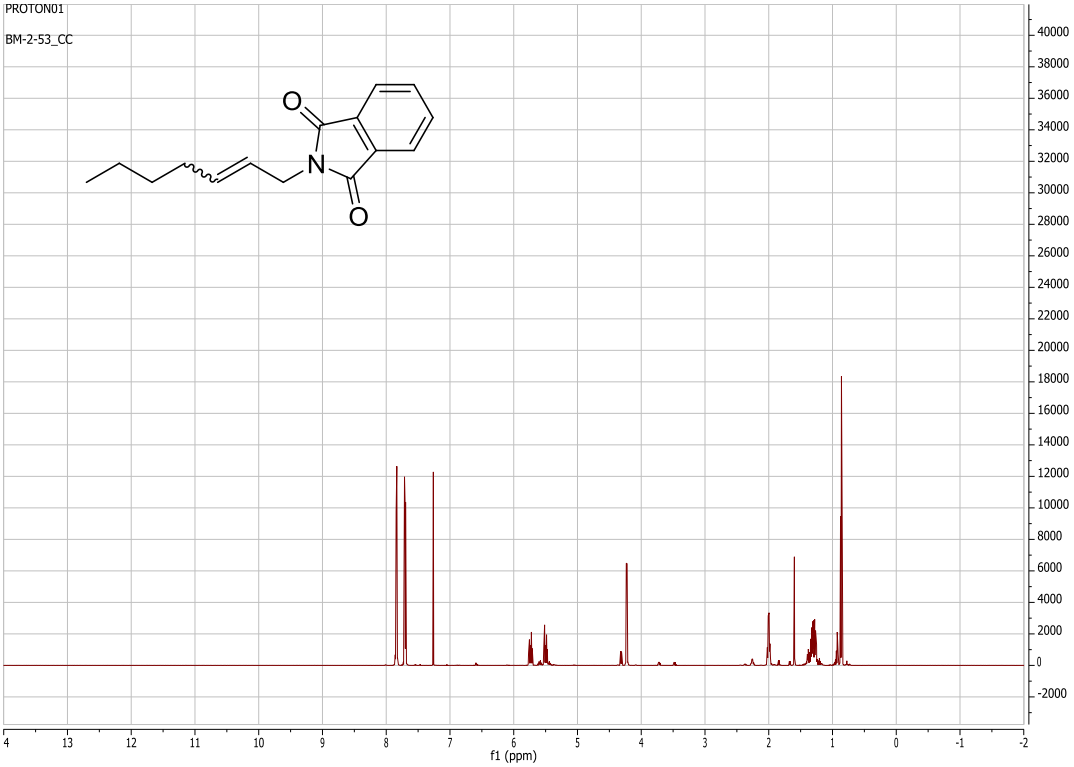

PROTON01
BM-2-57_CC
O
Me
NHTs
f1 (ppm)

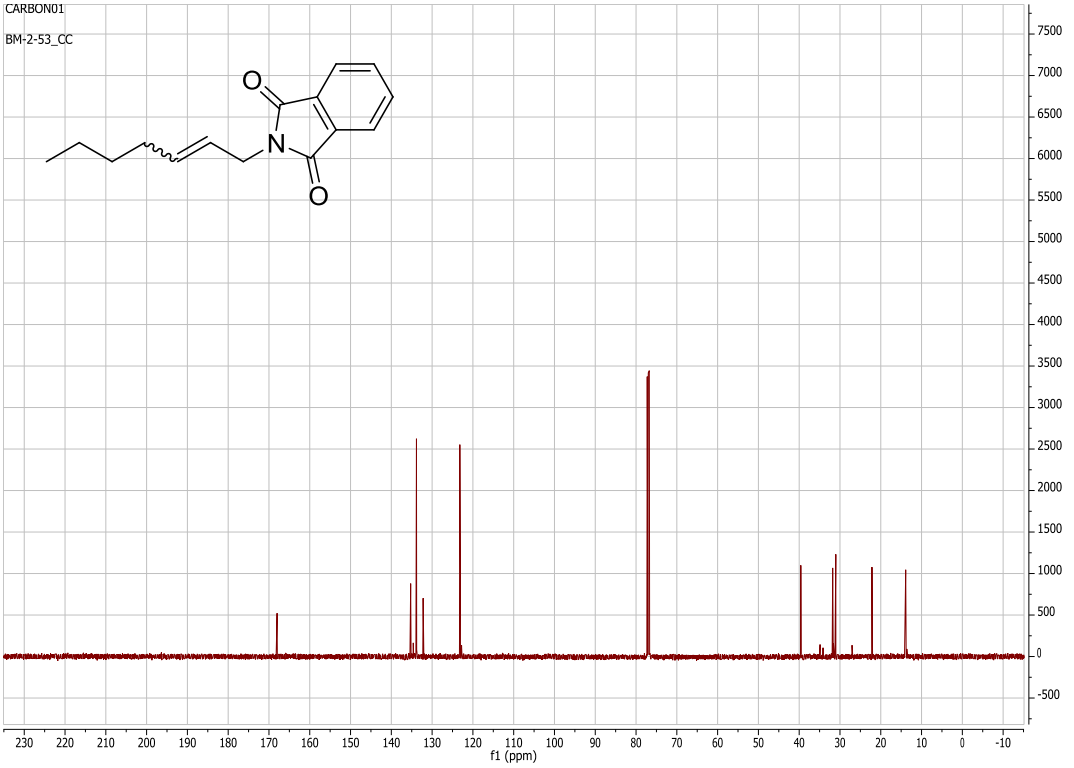

PROTON01
BM-280_CC
O
OMe
O
f1 (ppm)

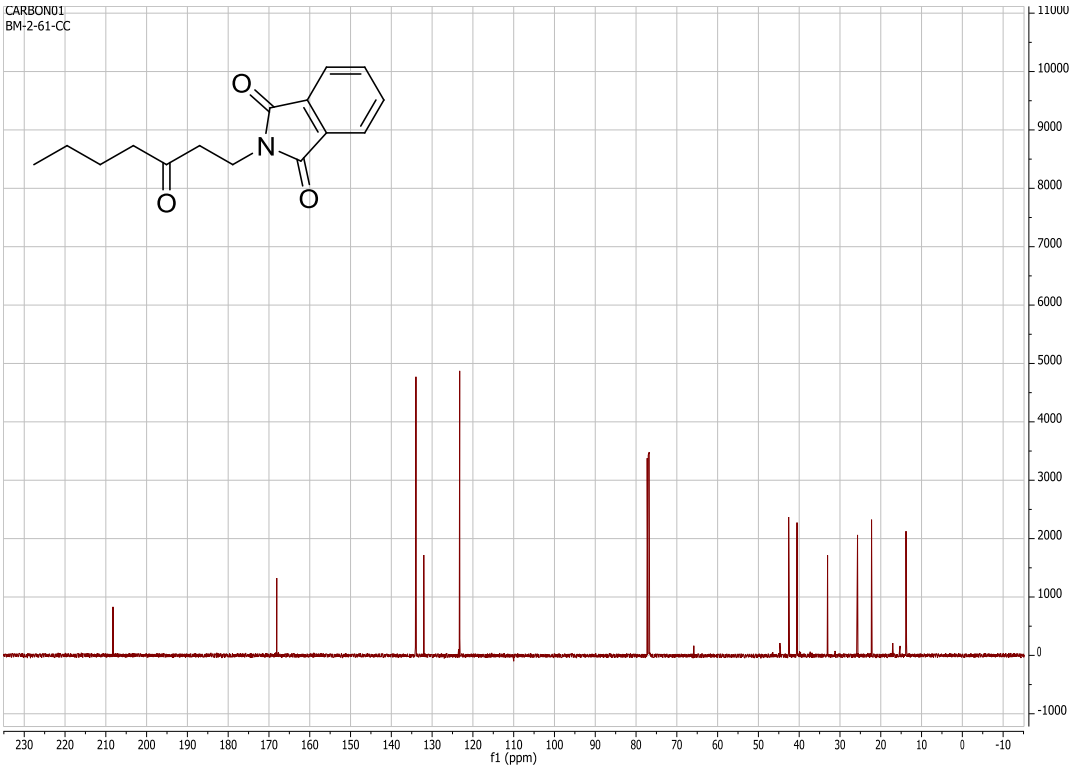

CARBON01
BM-280_carbon
O
OMe
O
f1 (ppm)

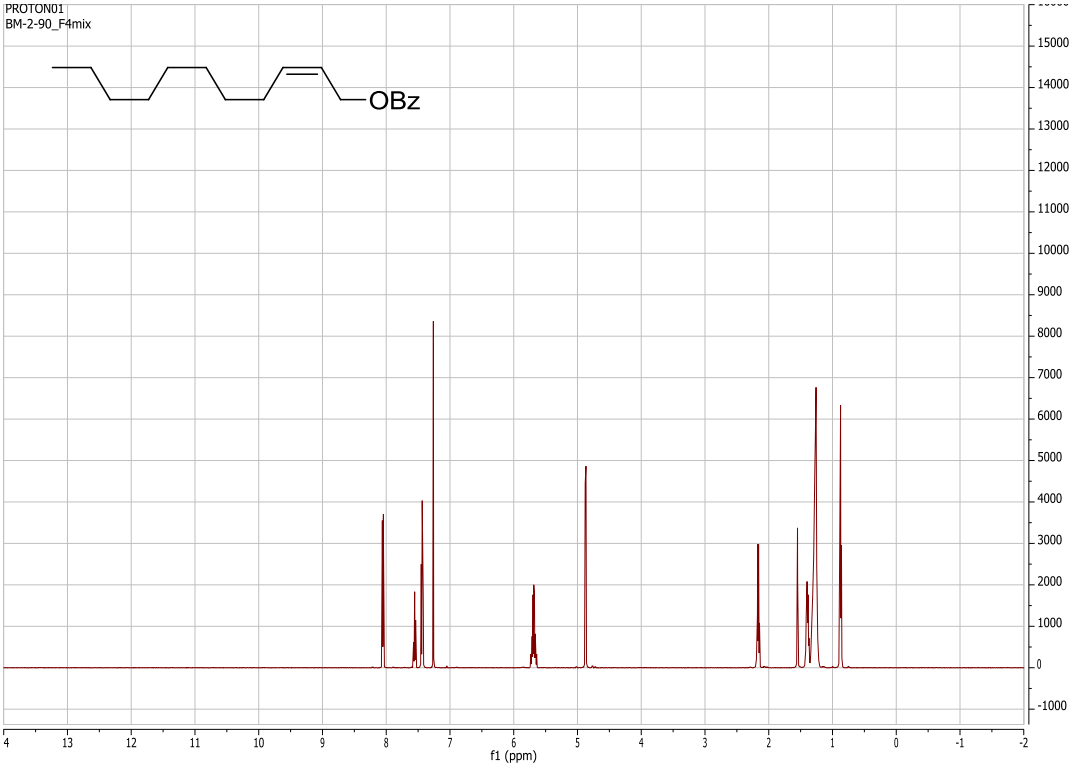

PROTON01
BM-2-50_CC
O
O
O
OMe
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
4
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)

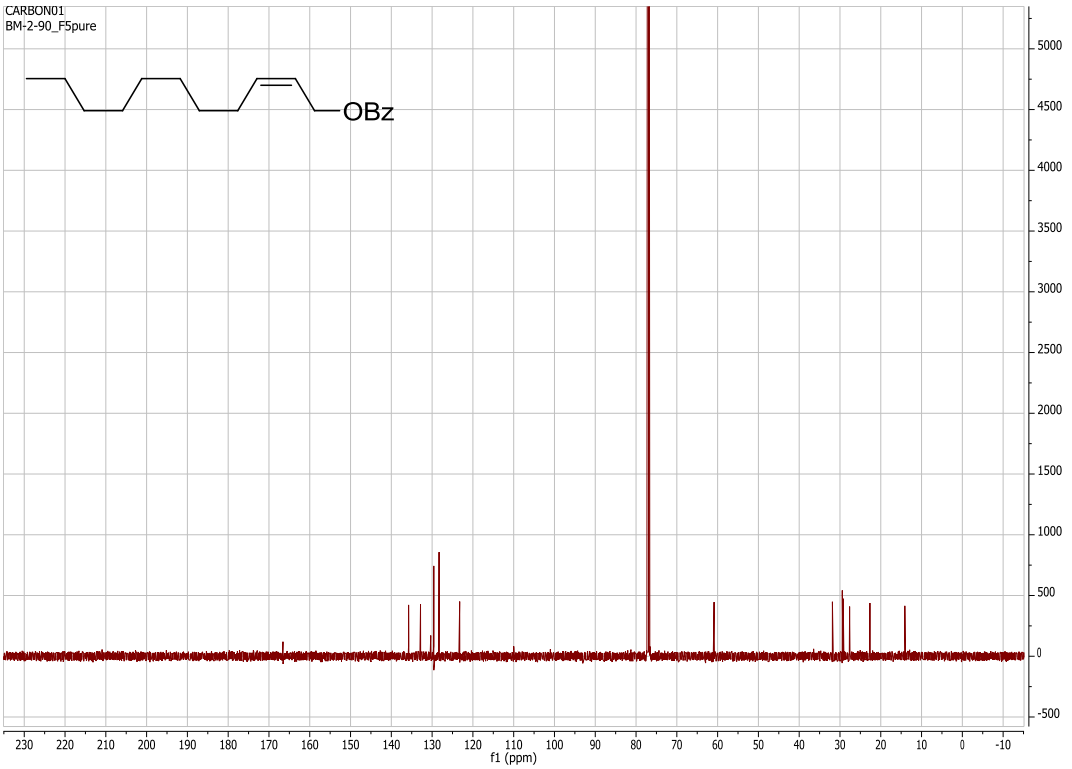

CARBON01
BM-2-50_CC
O
O
O
OMe
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

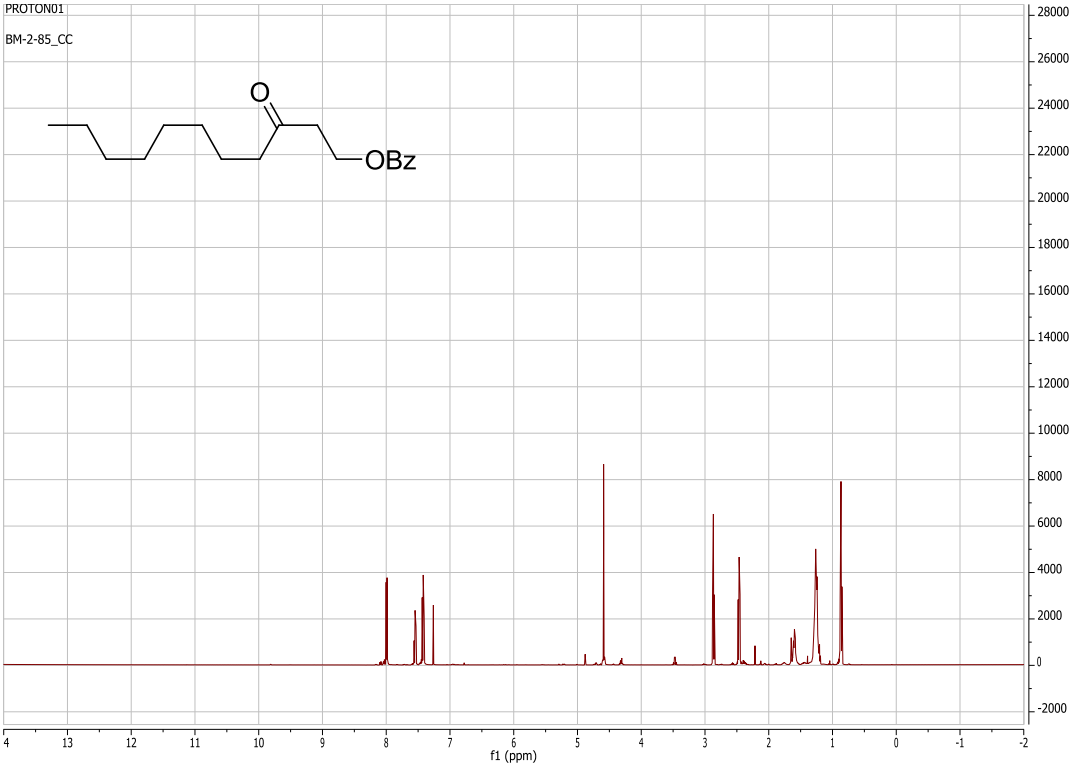

PROTON01
BM-2-53_CC
O
N
O
40000
38000
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
4
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)

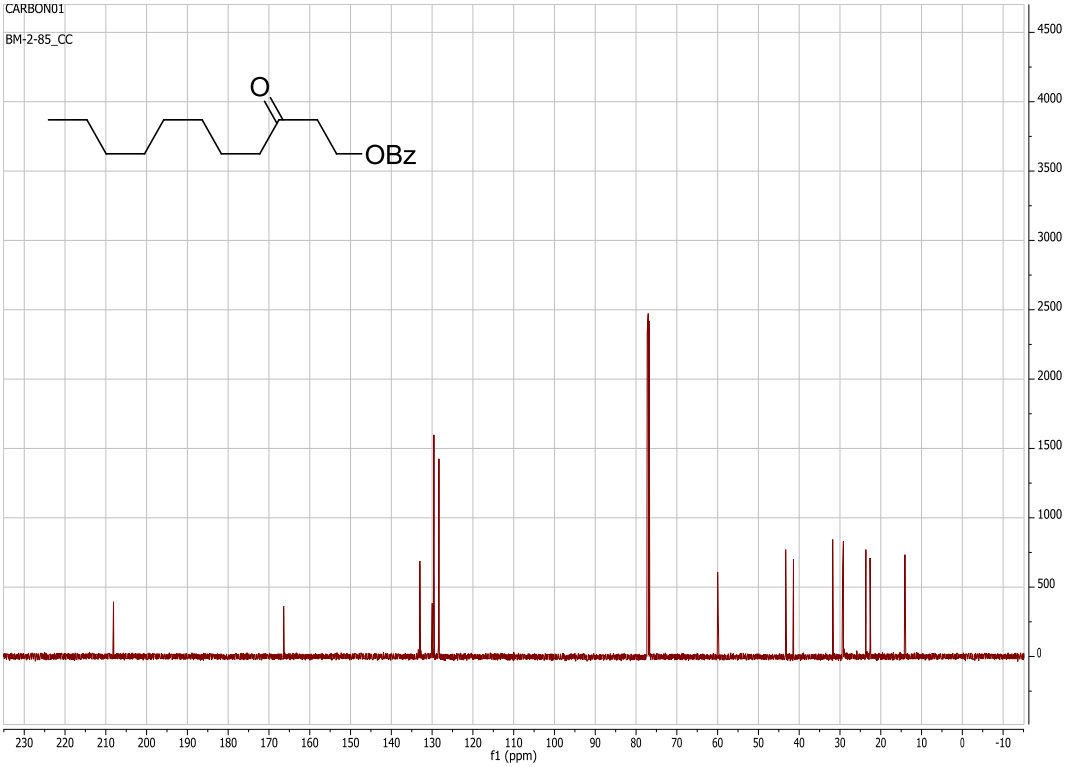

CARBON01
BM-2-53_CC
O
N
O
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

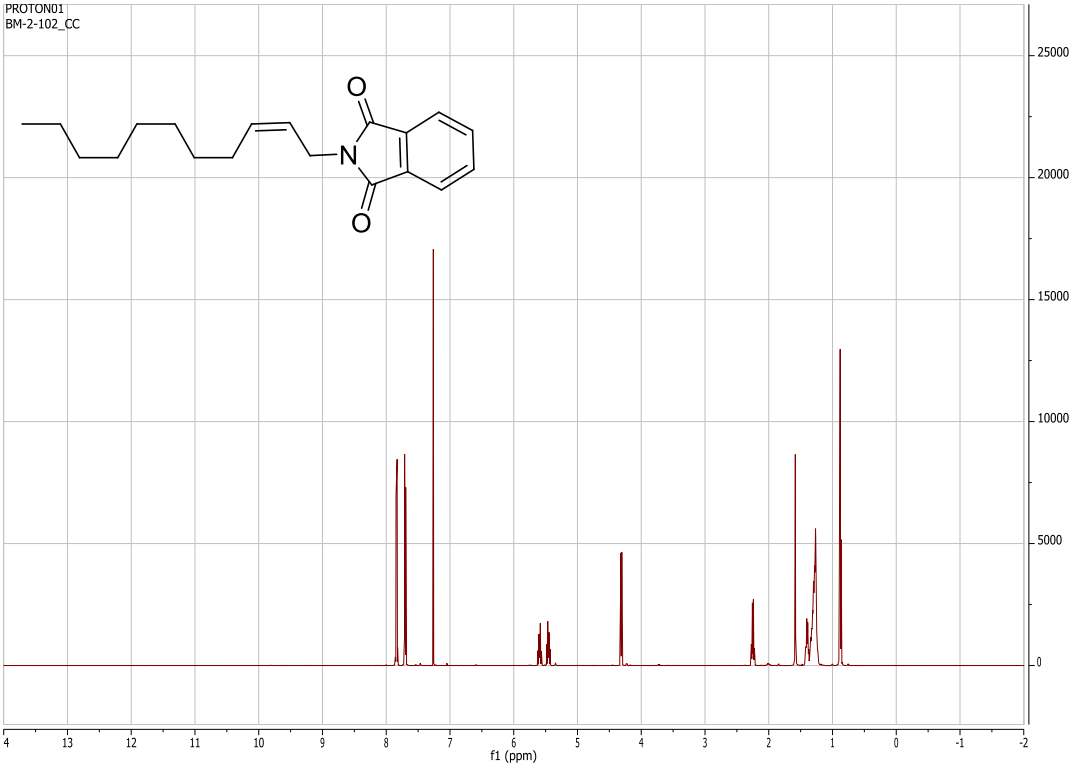

CARBON01
BM-2-61-CC
O
N
O
O
f1 (ppm)

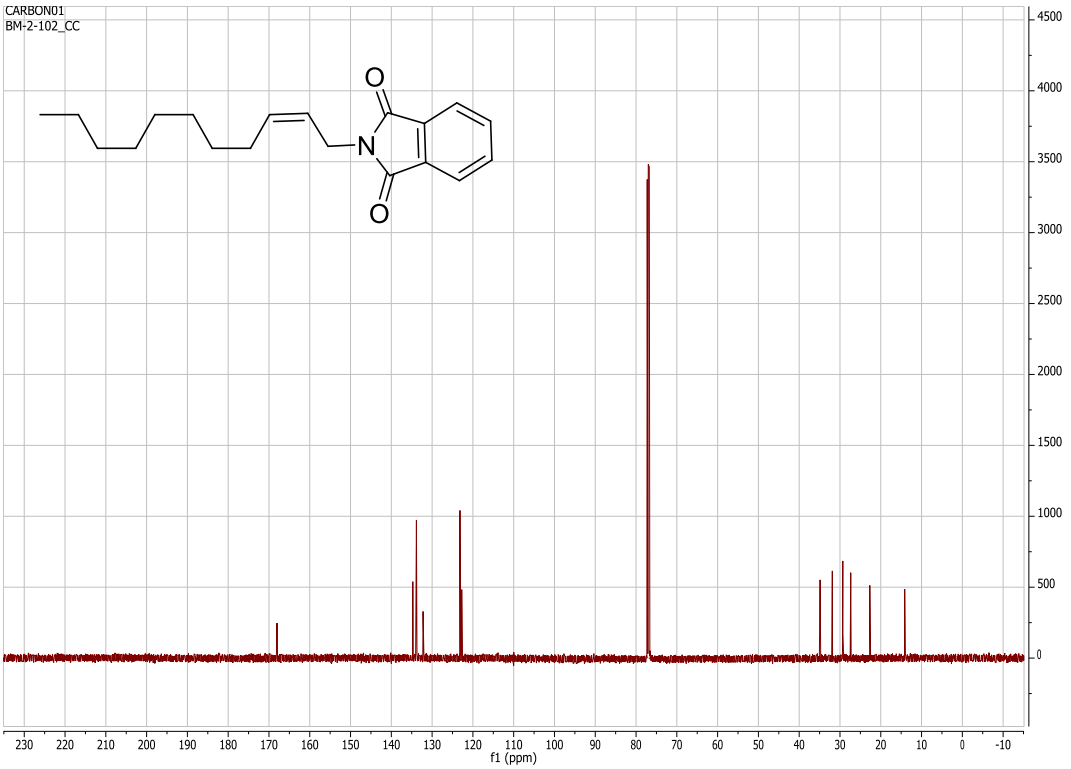

PROTON01
BM-2-90_F4mix
OBz
f1 (ppm)

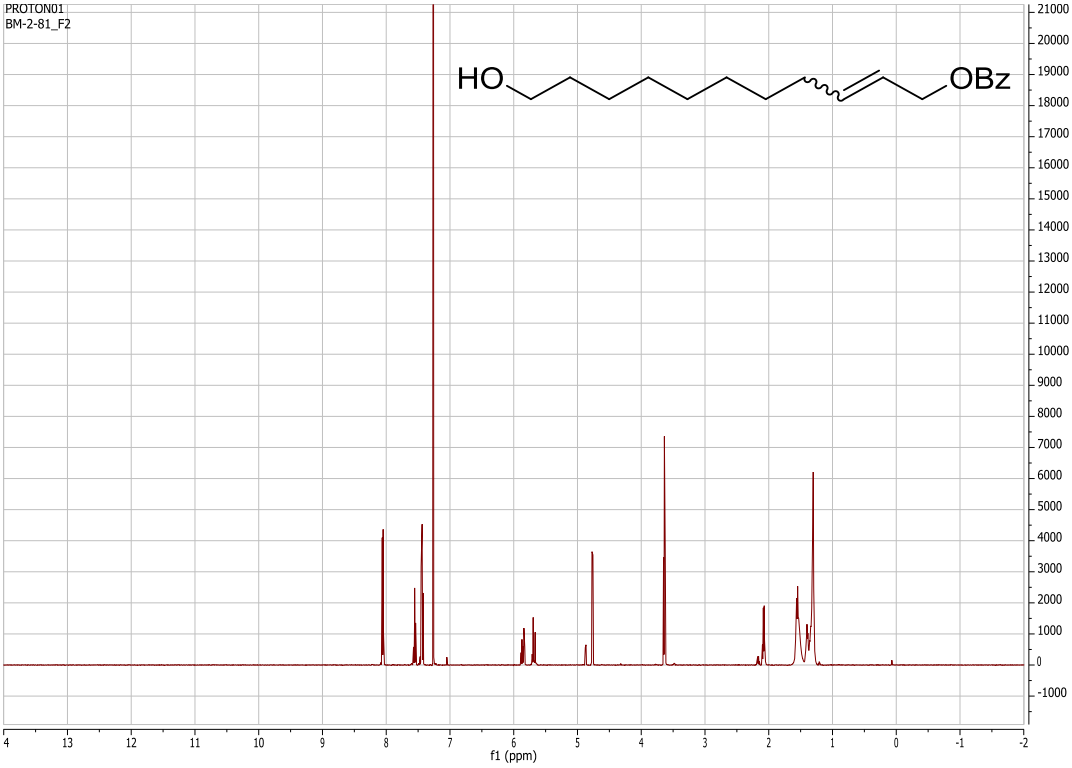

CARBON01
BM-2-90_F5pure
OBz
f1 (ppm)

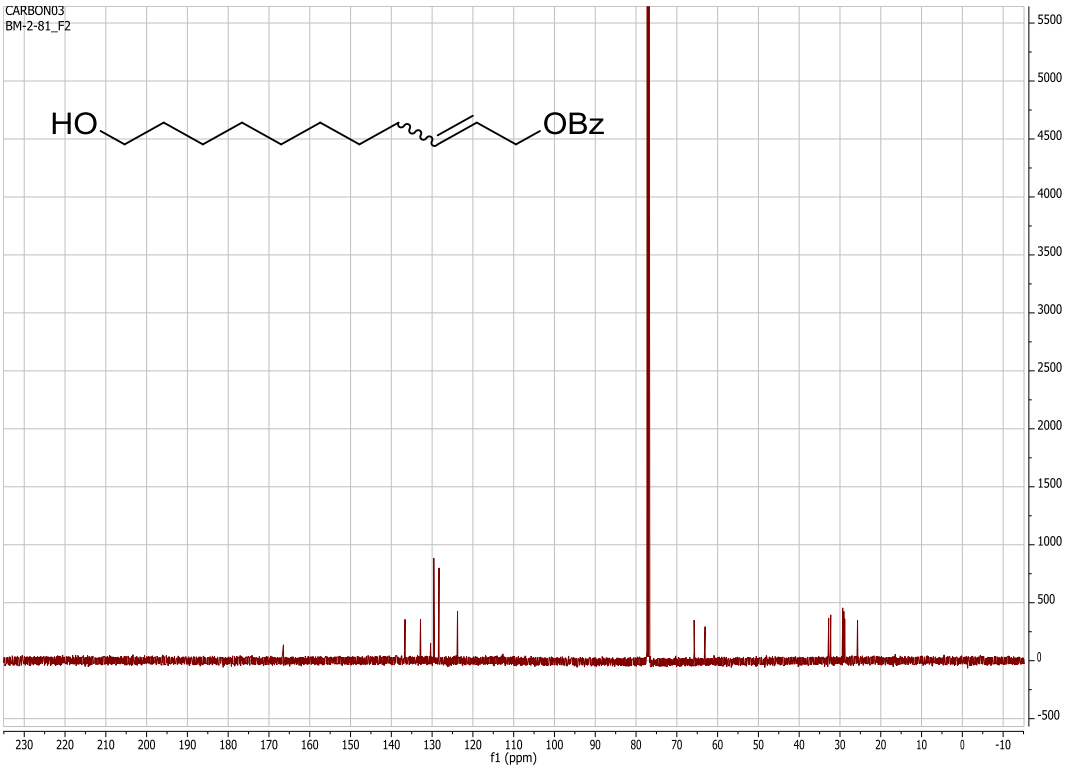

PROTON01
BM-2-85_CC
O
OBz
f1 (ppm)

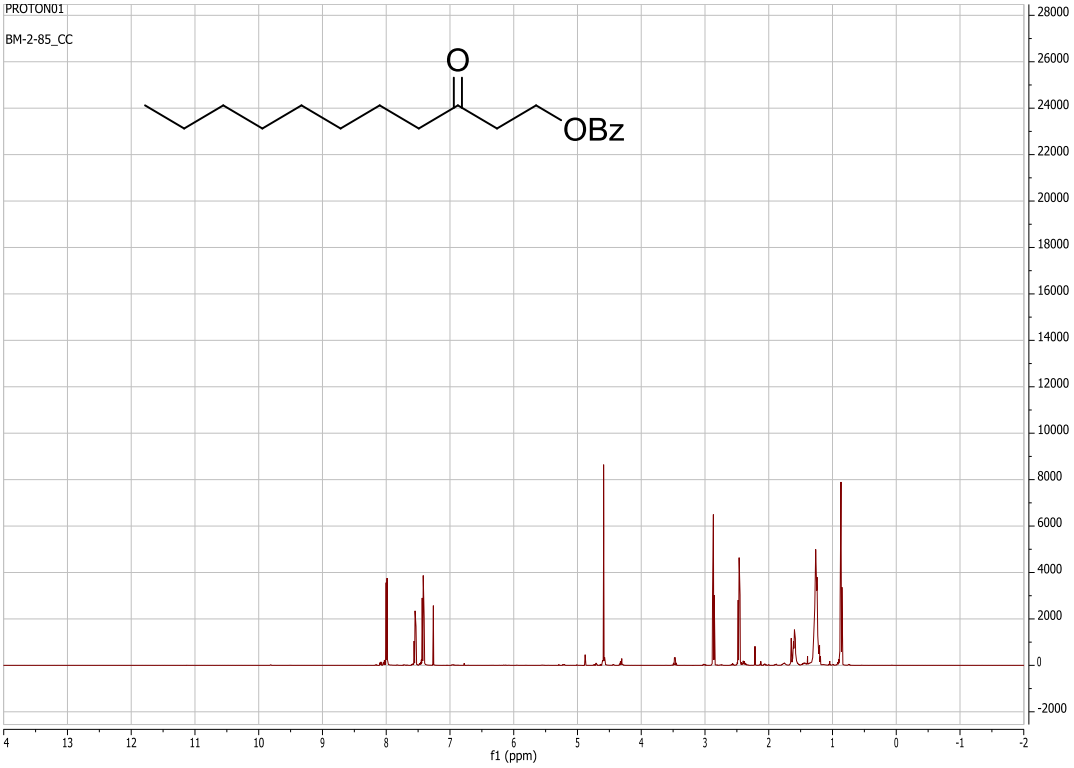

CARBON01
BM-2-85_CC
O
OBz
4500
4000
3500
3000
2500
2000
1500
1000
500
0
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

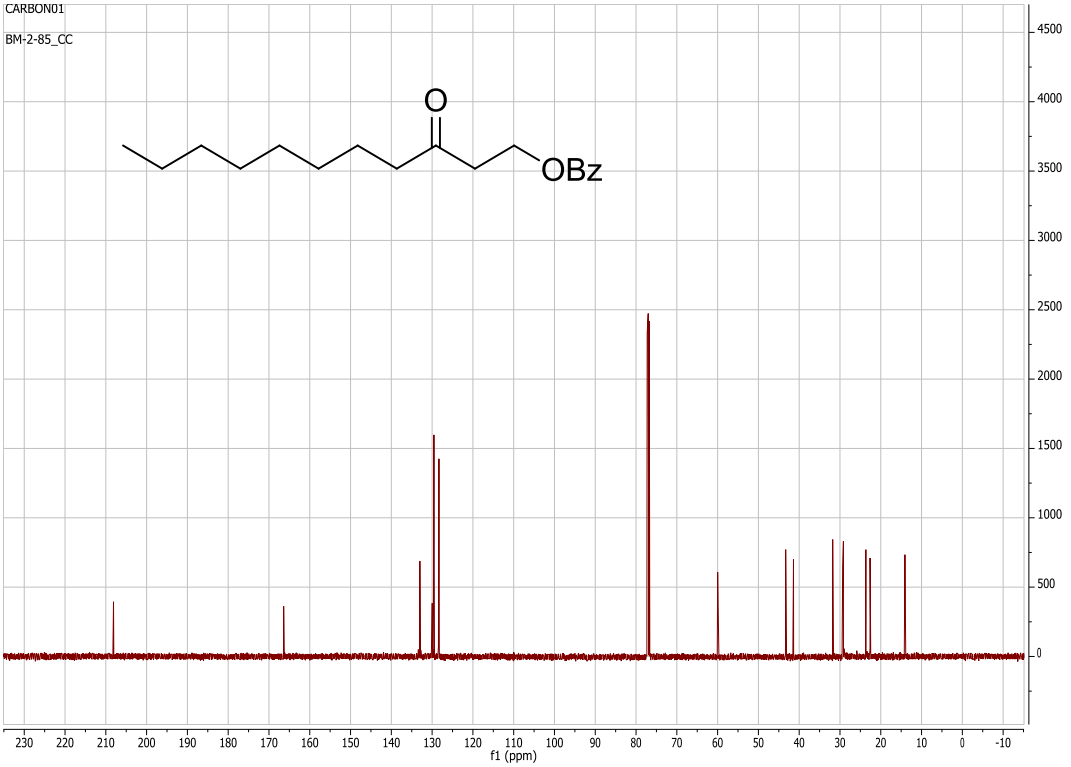

PROTON01
BM-2-102_CC
O
N
O
25000
20000
15000
10000
5000
0
4 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)

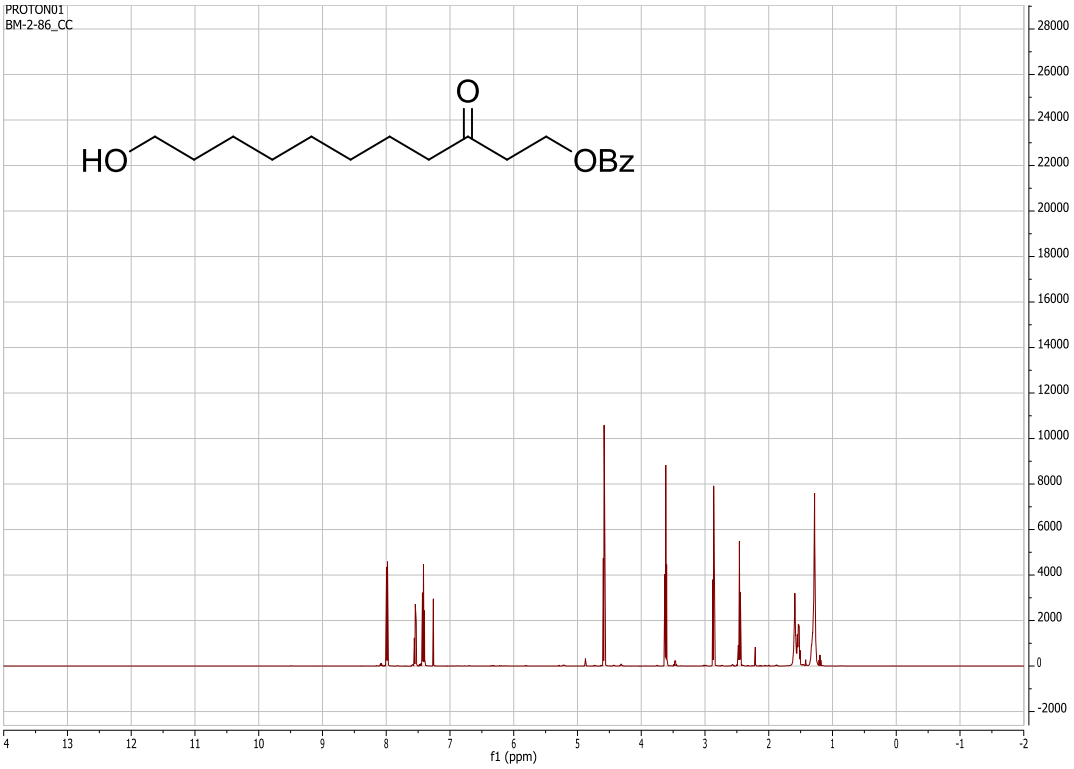

CARBON01
BM-2-102_CC
O
N
O
4500
4000
3500
3000
2500
2000
1500
1000
500
0
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

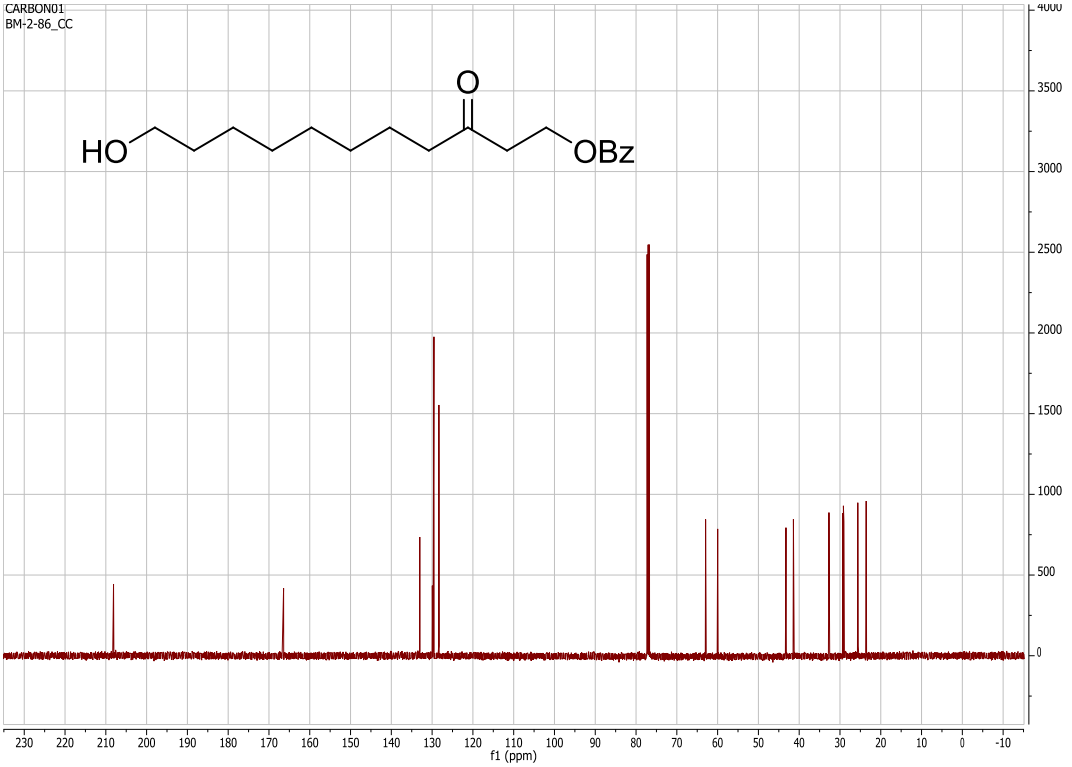

PROTON01
BM-2-81_F2
HO
OBz
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
4 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)

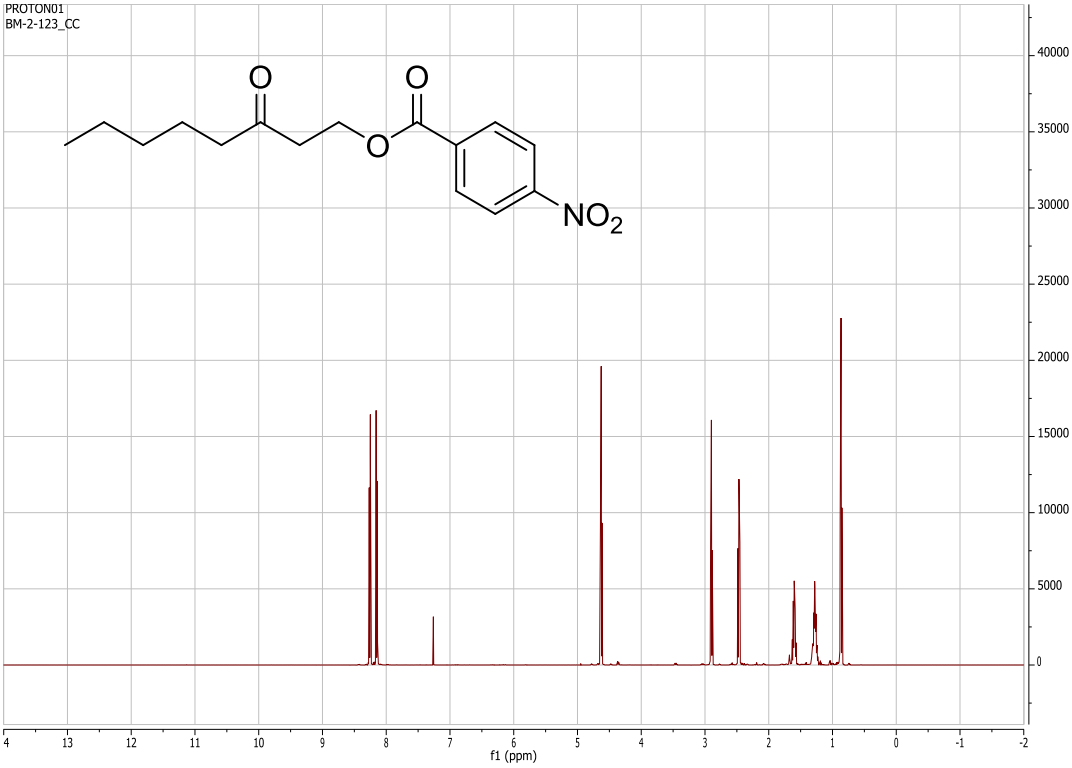

CARBON03
BM-2-81_F2
HO
OBz
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

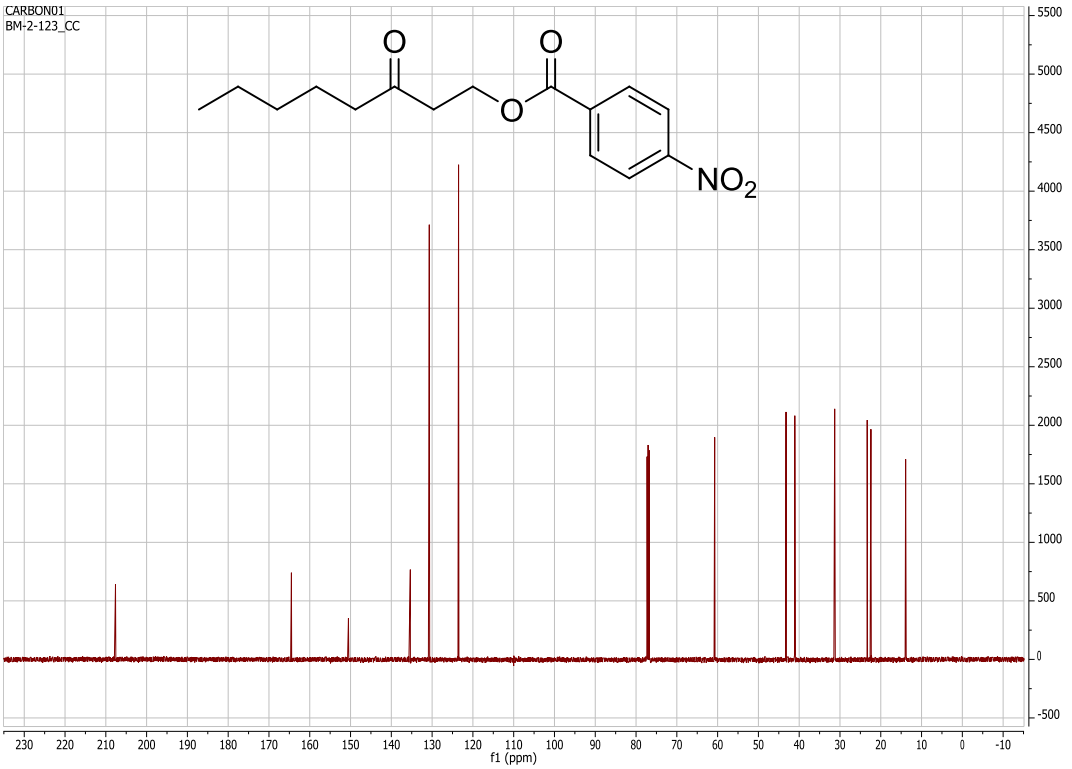

PROTON01
BM-2-85_CC
O
OBz
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
4 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)

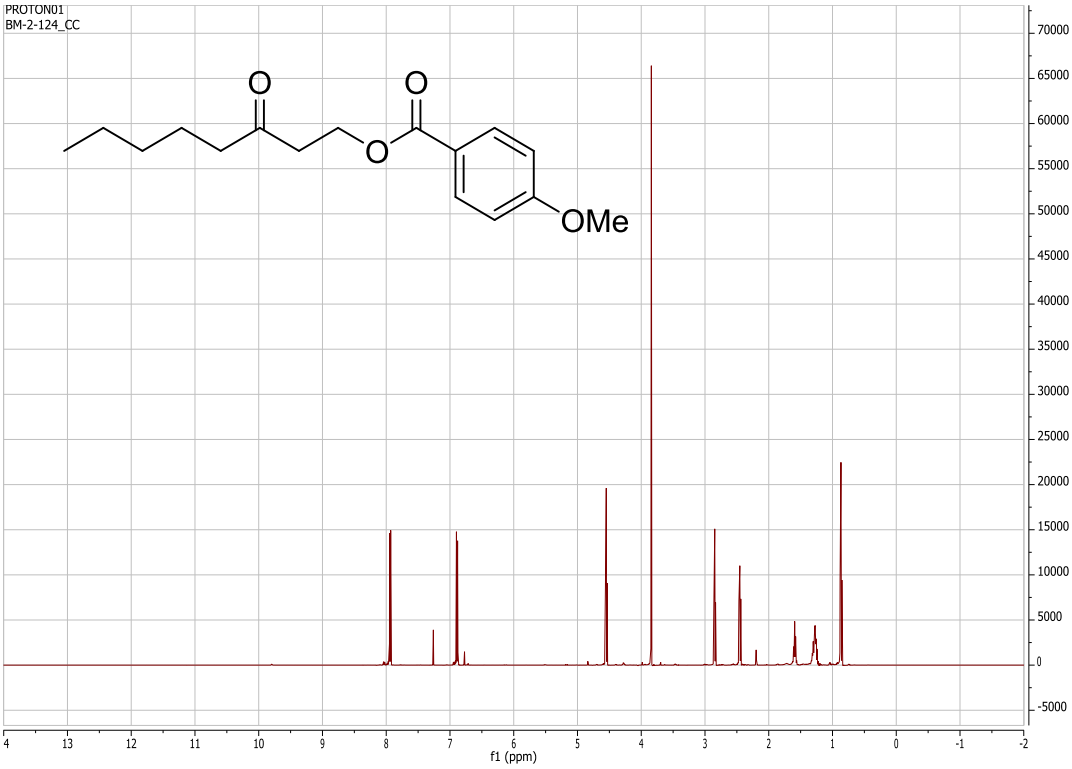

CARBON01
BM-2-85_CC
O
OBz
4500
4000
3500
3000
2500
2000
1500
1000
500
0
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

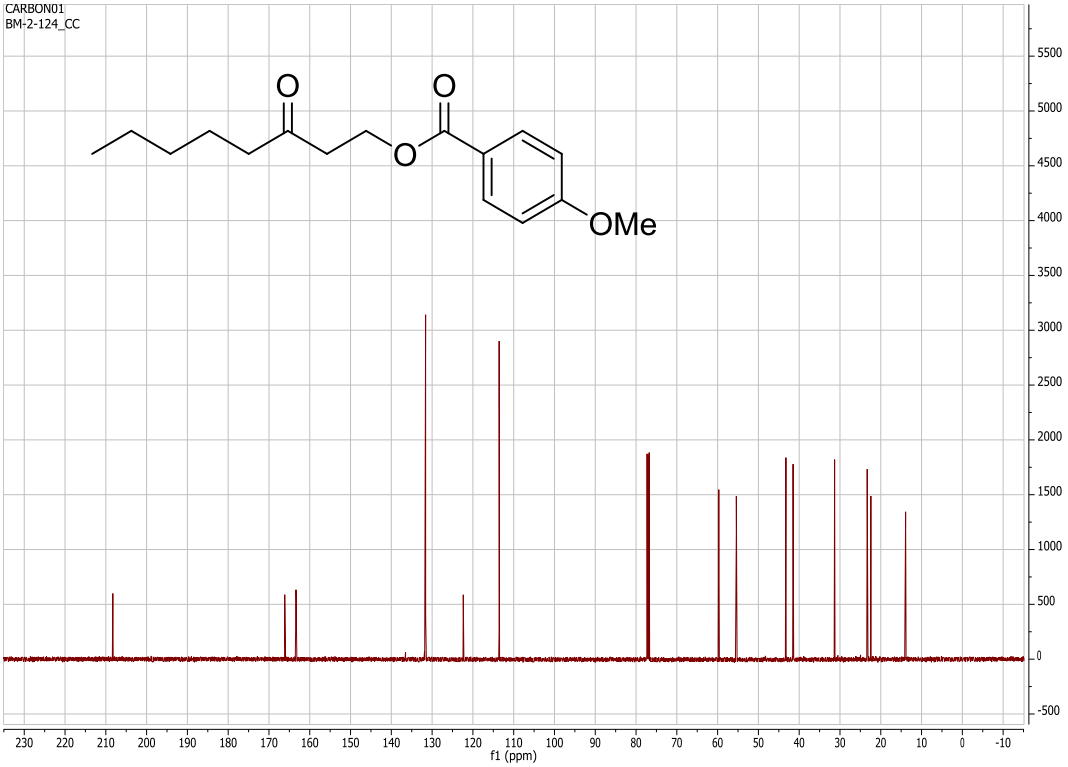

PROTON01
BM-2-86_CC
O
HO
OBz
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
4 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)


CARBON01
BM-2-86_CC
HO
O
OBz
f1 (ppm)


PROTON01
BM-2-123_CC
O
O
O
NO2
f1 (ppm)


CARBON01
BM-2-123_CC
O
O
O
NO2
f1 (ppm)


PROTON01
BM-2-124_CC
O
O
O
OMe
f1 (ppm)


CARBON01
BM-2-124_CC
O
O
O
OMe
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)